FULL PAPER

Nature of the synergy between Brønsted and Lewis acid sites in Sn-Beta zeolites for polyoxymethylene dimethyl ethers synthesis

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Abstract: The role of Lewis and Brønsted acid sites, and their potential synergy remains ambiguous for the production of polyoxymethylene dimethyl ethers (OME), which are suitable as Diesel substitute. Here, we studied this synergistic effect using a series of BEA zeolites with various degrees of Brønsted and Lewis acidity. Lewis acidity was introduced in dealuminated zeolites by Sn grafting in dichloromethane. These sites were only active in paraformaldehyde decomposition, OME growth, and acetalization. Brønsted acid sites arising from bridging hydroxyl groups were active for all reaction steps, and notably for trioxane ring-opening and dissociation to formaldehyde (FA), which did not occur on Lewis acid sites. Presence of both Lewis and Brønsted acid sites led to a four-fold increase in turnover frequency and a significant decrease of by-product formation compared to the parent zeolite during OME synthesis from OME₁ and trioxane. The synergistic effect between both types of acid sites is explained by FA insertion on Lewis acid sites leading to OME growth. Interaction between tetrahedral Sn and the carbonyl group of FA resulted in an activated carbonyl bond, which is likely to be the initial step for insertion of FA into OME.

Introduction

The transition to a carbon-free economy will lead to unprecedented changes in the transportation sector. However, Diesel engines will continue to power a large share of the vehicles in the near-future due to their high thermal efficiency and energy density, which are key requirements for heavy-duty transport. Diesel consumption is expected to grow between 46 and 200 % compared to its 2010 level during the next four decades, according to the World Energy Council.^[1] Meanwhile, air pollution has reached alarming levels in large cities forcing governments to adopt more stringent emission standards. In this context, polyoxymethylene dimethyl ethers (OME) have recently gained attention as a new type of Diesel additive or substitute due to their appealing properties.^[2,3] When blended with Diesel fuel, they reduce the level of soot emission with a concomitant increase in combustion efficiency.^[4–6] Moreover, their usage in diesel-powered cars only require slight engine modifications.^[4] Finally, they can be produced from

methanol which could be a future platform molecule synthesized from CO₂ or biomass.^[7,8]

The large-scale implementation of OME requires stable and active catalysts. Acidity is essential for OME synthesis and various solid acids have already been used as catalysts: acidic resins,^[9,10] zeolites^[11–13] or other aluminosilicate-based materials^[14,15]. Different synthesis routes exist depending on the oxymethylene and oxymethyl- sources:^[16] dimethoxymethane (OME₁), methanol or dimethyl ether, reacts with trioxane (TRI), formaldehyde (FA) or paraformaldehyde (PF) to form a Schulz-Flory (SF) distribution of OME. The anhydrous route demonstrated the highest OME yield, but synthesis from methanol and FA reduces production complexity.^[17,18]

Two reaction mechanisms were reported in the literature for OME synthesis: initiation, growth and termination (IGT) or sequential addition.^[16,19–21] The reactants and catalyst used determine which mechanism will prevail. The IGT mechanism is illustrated in Scheme 1. Initiation happens through the generation of a carbocation or a hemiformal intermediate. In the anhydrous route, OME₁ forms a carbocation on a Brønsted site, whereupon methanol is released. Alternatively, methanol reacts rapidly with FA to generate a hemiformal. Growth occurs then by insertion of FA units into the above mentioned intermediates.^[21] FA units can be generated from the decomposition of TRI or PF, but insertion of TRI into OME has also been reported.^[21] In their intermediate carbocation form, two OME can also exchange FA units (transacetalization reaction). Finally, termination occurs when methanol reacts with a hemiformal to produce OME and water (acetalization reaction). In the anhydrous route, the termination reaction is the reverse reaction of the initiation. The other reaction mechanism proposed is the sequential addition, which is similar to the growth step of IGT, except that OME are not in an intermediate form.^[12]

Scheme 1. OME synthesis following the IGT mechanism from methanol or OME₁.

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Various studies demonstrated that strong Brønsted acidity was required for OME synthesis.^[22,23] Others showed that Lewis acidity could also catalyze OME production.^[24,25] However, these studies implied a wide range of reactants and catalysts, which prevents general conclusions to be drawn.

Liu et al. recently reported the existence of a synergy between Lewis and Brønsted acid sites for the synthesis of OME from PF and OME₁.^[26] However, their suggested reaction mechanism does not explain the nature of this synergistic effect. Thus, the precise role of Brønsted and Lewis acid sites, and their potential synergy remains ambiguous. Therefore, the goals of this study were twofold. First, we sought to acquire a deeper understanding of the type of acidity involved in the different OME synthesis steps. Second, we aimed at investigating the nature of the synergy between Lewis and Brønsted acid sites. These objectives were pursued by synthesizing a series of BEA zeolites with various amounts of Brønsted and Lewis acid sites (Scheme 2).

Lewis acidity was introduced in the zeolite framework via Sn incorporation by grafting in dichloromethane, as it was shown to lead to high and controllable Sn content with little extra-framework Sn.^[27] These catalysts were then applied in several reactions for OME synthesis. The results of this work demonstrated that Brønsted sites were active in all steps of OME synthesis while Lewis acid sites were only active in OME growth, PF decomposition and hemiacetal acetalization. Our study also confirmed the synergy between Brønsted and Lewis sites, and identified FA insertion in OME on tetrahedral Sn as the key step involving Lewis sites.

Results

Physico-chemical characterization of the catalysts

Neither dealumination, nor Sn grafting affected the zeolite structure, as all XRD patterns were consistent with the BEA topology (Fig. S1, Supplementary information). Furthermore, no SnO₂ phase was detected, which rules out the possibility of the presence of extra-framework crystallites larger than 3 nm.

Scheme 2. Treatments applied to parent H-Beta zeolite (H-Beta-P) for the synthesis of a series of zeolites with varying amounts of Brønsted and Lewis acid sites.

The textural properties were assessed by N₂ physisorption measurements (Table 2) and no structure amorphization was identified following the treatments of the zeolites.

The protonated parent zeolite (H-Beta-P) displayed initial mesoporosity (172 m²·g⁻¹), which increased with the dealumination treatment to 189 and 192 m²·g⁻¹ for 2-DeAl and 14-DeAl, respectively. Dealumination also induced a slight increase in H-Beta-P microporous surface area (*S*_{micro}) from 356 m²·g⁻¹, to 379 and 400 m²·g⁻¹ for 2-DeAl and 14-DeAl, respectively. Sn grafting resulted in a small decrease in *S*_{micro}, while the mesoporous surface area decreased with increasing the Sn grafting concentration.

Table 1. Textural parameters, composition and acidity of the catalysts.

Sample	Surface area (m ² ·g ⁻¹)			Volume (cm ³ ·g ⁻¹)		Composition (wt. %)			
	BET	Micro ^[a]	Meso ^[b]	Micro ^[a]	Meso ^[b]	Al	Si	Sn	Acidity (mmol·g ⁻¹)
H-Beta-P	543	356	172	0.155	0.536	3.50	41.40	0	0.880
2-DeAl	589	379	189	0.166	0.655	0.35	43.31	0	0.196
14-DeAl	609	400	192	0.174	0.638	0.05	43.41	0	0.081
0.5Sn-2-DeAl	554	348	188	0.150	0.694	0.35	43.46	0.28	0.187
2Sn-2-DeAl	567	361	184	0.158	0.655	0.35	43.78	0.63	0.193
10Sn-2-DeAl	556	357	182	0.156	0.621	0.35	43.55	1.09	0.225
50Sn-14-DeAl	558	352	183	0.152	0.610	0.05	45.00	3.06	0.230

[a] Calculated based on the t-plot method. [b] Calculated based on the BJH method using the adsorption branch.

Fig. 1. ICP-OES analysis of the various catalysts.

ICP-OES analysis (Fig. 1) confirmed that the aluminum concentration decreased with an increasing dealumination extent, changing from 3.5 to 0.35 wt. % with partial dealumination. Complete dealumination led to removal of almost all Al content (0.046 wt. % left). Increasing Sn loadings were achieved for the partially dealuminated, Sn-modified samples with increasing SnCl_4 concentration during Sn grafting. The highest Sn content of 3.06 wt. % was reached with 50Sn-14DeAl, which thus mainly contained Sn compared to Al (Sn/Al molar ratio of 13.41). DRIFT spectroscopy confirmed that Sn was incorporated into the zeolite framework in vacant silanol nests (Fig. S2). Aluminum

extraction led to an increase in the terminal Si-OH and internal silanol nest signals, respectively at 3740 and ca. 3500 cm^{-1} .^[33] The silanol nest signal decreased with increasing Sn loading, while the isolated silanol signal did not vary. The Sn distribution in the zeolite framework was also examined by HAADF-STEM imaging with elemental mapping (Fig. S3). Sn was well dispersed in all Sn-containing samples and no aggregates were observed. Next, Sn coordination states in the Sn-modified samples were studied by XPS (Fig. 2a). Overall, the two signals derived from the $3d_{5/2}$ and $3d_{3/2}$ were close to previously reported values corresponding to tetrahedrally coordinated framework Sn (487.4 eV and 495.8 eV).^[34] No signal caused by octahedral Sn was detected at 486.0 and 494.4 eV which shows that no extra-framework Sn was present in these catalysts. Diffuse reflectance UV-Vis (DRUV) spectroscopy also confirmed that no extra-framework Sn was present as no signal was obtained around 280 nm, which has been attributed to extra-framework SnO_2 (Fig. 2b).^[35] The main signal was located between 218 and 235 nm, arising from the ligand-to-metal charge transfer from the surrounding O atoms to the unoccupied orbitals of isolated Sn^{IV} .^[36]

The Sn-containing samples were further characterized by ^{119}Sn magic angle spinning NMR (MAS-NMR) (Fig. S4a and b). 50Sn-14-DeAl, which contained the highest Sn load, displayed a peak centered at -616 ppm, which corresponds to the hydrated form of Sn in a tetrahedral coordination in the framework lattice.^[37] Due to their smaller loadings and the low abundance of ^{119}Sn , for the partially dealuminated, Sn-modified samples Carr–Purcell–Meiboom–Gill (CPMG) MAS-NMR analysis were applied. This resulted in a sharper peak located at -643 and -650 ppm for 2Sn-2-DeAl and 10Sn-2-DeAl, respectively. This signal is attributed to hydrated, hydrolyzed open Sn sites, which are expected after Sn grafting on a dealuminated zeolite.^[27,37]

Fig. 2. Analysis of the Sn-containing catalysts by (a) XPS and (b) in-situ DRUV spectroscopy at 400 °C under a He flow of 20 $\text{mL} \cdot \text{min}^{-1}$. The gray and colored lines correspond to the original and smoothed curves, respectively. Smoothing was performed using a FFT filter (5 points).

Fig. 3. Characterization of the acidity of the various catalysts by (a) NH_3 -TPD and (b) pyridine-FTIR spectroscopy at various temperature (H indicates H-bonded pyridine, while L and B respectively indicate pyridine bonded to Lewis and Brønsted sites).

Sn concentration in 0.5Sn-2DeAl was too low to acquire an effective signal and is thus not displayed. However, due to the similarity in the grafting method, we suggest that Sn coordination to the framework is similar to the other dealuminated samples. Overall, these characterization results indicate that Sn grafting resulted in the incorporation of Sn in a tetrahedral coordination within the dealuminated BEA framework.

Samples acidity was quantified by NH_3 -TPD (Fig. 3a, Table 1). Overall, partial dealumination reduced the acid sites concentration from 0.880 to 0.196 $\text{mmol}\cdot\text{g}^{-1}$ for H-Beta-P and 2-DeAl, respectively. 14-DeAl contained a residual acidity of 0.081 $\text{mmol}\cdot\text{g}^{-1}$. Meanwhile, the acidity of the partially dealuminated, Sn-modified samples increased proportionally to the Sn loading. Sn grafting on 14-DeAl resulted in the appearance of a peak centered around 200 °C in its NH_3 -TPD profile and increased its acidity to 0.230 $\text{mmol}\cdot\text{g}^{-1}$, close to the acidity of 10Sn-2-DeAl (0.225 $\text{mmol}\cdot\text{g}^{-1}$). The nature and strength of the catalysts acid sites were studied by infrared spectroscopy of adsorbed pyridine (Fig. 3b). Characteristic vibrational bands of H-bonded pyridine (1444 and 1596 cm^{-1}), and pyridine bonded to a Brønsted (1530 cm^{-1}) or a Lewis site (1451 and 1610 cm^{-1}) were detected.^[38] Comparison of H-Beta-P and 2-DeAl spectra shows that dealumination did not affect the strength of Brønsted acid sites as the signal intensity remained constant with increasing temperatures. Notably, all dealuminated samples displayed a higher signal due to H-bonded pyridine to silanol groups. 0.5Sn-2-DeAl, 2Sn-2-DeAl and 10Sn-2-DeAl all displayed Brønsted and Lewis acidity while 50Sn-14-DeAl only exhibited Lewis acidity. Signals corresponding to Lewis acid sites were more clearly observed for 50Sn-14-DeAl and 10Sn-2-DeAl due to the higher Sn content. The signals assigned to Lewis sites of Sn-modified samples slightly decreased with increasing temperatures and thus correspond to a moderate acid strength. Overall, H-Beta-P

and 2-DeAl contained strong Brønsted sites, 50Sn-14DeAl possessed moderate Lewis acidity, and the partially dealuminated, Sn-modified samples contained strong Brønsted and moderate Lewis acidity. The latter is thus provided from tetrahedral Sn incorporated in the dealuminated framework.

Catalytic performance screening for various OME synthesis reactions

In order to elucidate the role of Lewis and Brønsted acid sites during the various steps of OME synthesis, the synthesized catalysts were used for the reactions described in Scheme 3: OME₁ and TRI (R1), OME₁ and PF (R2), FA and MeOH (R3) and OME₂ equilibration (R4).

Scheme 3. Various reactions performed for the synthesis of OME. The different sources of formaldehyde are displayed in red.

First, TRI and OME₁ (R1) were used as reactants (Fig. 4a). A decrease in activity was observed with an increase in dealumination extent. Addition of Lewis acid sites on the completely dealuminated zeolite did not increase the sample activity as 14-DeAl and 50 Sn-14-DeAl had similar minor TRI conversion and formaldehyde concentration. Compared to 2-DeAl, catalysts displaying both Brønsted and Lewis sites had a much higher activity, comparable to H-Beta-P, despite their much lower concentration of acid sites.

The synthesis of OME using PF and OME₁ (R2) displayed results similar to R1 with a large increase in activity when both Lewis and Brønsted sites were present (Fig. 4b). However, two differences were noticed. First, dealumination had a more severe effect on the performance; 2-DeAl reached a OME₂₋₈ concentration of only 0.70 mol·L⁻¹, compared to 2.86 mol·L⁻¹ for H-Beta-P. Second, 50Sn-14-DeAl had a notably better performance (0.56 mol·L⁻¹) compared to 14-DeAl (0.05 mol·L⁻¹), but still much lower compared to H-Beta-P. Lewis acid sites were thus active in R2, but less than Brønsted acid sites, as more OME were produced using 2-DeAl than 50Sn-14-DeAl, despite the larger acid site concentration of the latter.

Next, the synthesis of OME from FA and MeOH (R3, Fig. 4c) was performed. The effect of dealumination on the performance was more severe on the catalyst performance compared to R1 and R2. After 16 h, 2-DeAl and 14-DeAl respectively reached a OME₂₋₈ concentration of 0.15 and 0.05 mol·L⁻¹, compared to 3.01 mol·L⁻¹ for H-Beta-P. Meanwhile, no clear increase in activity was observed when both Brønsted and Lewis sites were present; 0.5Sn-2-DeAl had performance comparable to 2-DeAl. However, Lewis acid sites also contributed to OME synthesis, as 2Sn-2-DeAl, 10Sn-2-DeAl and 50Sn-14-DeAl had an activity superior to the dealuminated samples. The presence of water, produced in large amounts from reaction R3, seemed to affect Lewis acid sites more severely than Brønsted acid sites, as the results after 48 h showed a higher relative increase for all samples containing Brønsted acid sites compared to 50 Sn-14DeAl bearing only Lewis acid sites.

To gain a better insight into the role of Lewis acid sites, OME₂ equilibration into a SF distribution of OME (R4) was performed. This reaction also requires OME activation on an acid site for FA units to be transferred between different OME. It occurs under anhydrous conditions, similarly to R1, but does not involve TRI decomposition. Therefore, a SF distribution of OME was obtained from OME₂ when exposed to an acidic catalyst. Fig. S5 demonstrates this effect with H-Beta-P: OME of various chain length were obtained as OME₂ concentration decreased to reach a SF distribution. The rates of OME₂ equilibration over the different catalysts followed the trend: H-Beta-P > 2-DeAl > 0.5Sn-2-DeAl > 14-DeAl > 50Sn-14-DeAl (Fig. 5). As Sn-modified catalysts have lower performance compared to their dealuminated counterparts, it is clear that Brønsted acidity is required to activate OME for the equilibration reaction R4, while Lewis acidity is insufficient for this purpose.

Fig. 4. Synthesis of OME using various catalysts: (a) TRI conversion X_{TRI} and FA concentration using OME₁ and TRI ($T = 30\text{ }^{\circ}\text{C}$, 0.5 wt. % catalyst, reaction time of 20 min, molar ratio OME₁:TRI = 3.3), (b) OME₂₋₈ concentration using OME₁ and PF ($T = 60\text{ }^{\circ}\text{C}$, 0.5 wt. % catalyst, reaction time of 20 min, molar ratio OME₁:FA = 1.1), and (c) OME₂₋₈ concentration using FA and MeOH ($T = 80\text{ }^{\circ}\text{C}$, 1.0 wt. % catalyst, molar ratio MeOH:FA = 2.0).

Fig. 5. Equilibration of OME_2 (99.0 %) into OME_n using various catalysts ($T = 25^\circ\text{C}$, 1.0 wt. % catalyst) (bottom). The reaction was performed at a larger time-scale for 14-DeAl and 50Sn-14-DeAl (top).

TRI decomposition in DCM was performed using various catalysts in order to understand the interaction of grafted Sn with TRI in the absence of OME_1 (Fig. 6). TRI decomposition increased with an increasing Al content: H-Beta-P reached a TRI conversion of 0.34 compared to 0.26 and 0.13 for 2-DeAl and 14-DeAl, respectively. Addition of Sn in the zeolite framework at low concentrations did not alter the conversion significantly: 0.5Sn-2-DeAl and 2Sn-2-DeAl reached a TRI conversion of 0.26 and 0.24, respectively. However, at higher Sn concentrations, TRI conversion increased by 31 and 29% for 50Sn-14DeAl and 10Sn-2DeAl, respectively, compared to their dealuminated counterparts. Meanwhile, MF production augmented with increasing Sn content for partially dealuminated, Sn-containing zeolites. However, the combination of Brønsted and Lewis sites resulted in the highest MF production among Sn-containing zeolites. Notably, 50Sn-14-DeAl produced approximately half the amount of MF compared to 10Sn-2-DeAl despite the same total acidity and a three-fold Sn concentration in the zeolite. It thus appears that Brønsted acid sites were considerably more active for the TRI decomposition compared to Lewis acid sites. Presence of Sn resulted in the production of MF, especially when combined with Brønsted acid sites.

Overall, strong Brønsted acid sites resulting from bridging hydroxyl groups were active for all reactions performed. For catalysts containing only Brønsted acidity, an increasing extent of dealumination always led to a decrease in catalytic performance. In contrast, moderate Lewis acid sites resulting from tetrahedral Sn were inactive for R1 and R4, but still provided moderate activity for R2 and R3. When both Brønsted and Lewis acid sites were present, in combination with OME_1 and a source of formaldehyde, a large increase in activity was observed which is ascribed to a synergistic effect between both acid sites.

Fig. 6. TRI conversion X_{TRI} and MF concentration for the TRI decomposition in DCM using various catalysts ($T = 70^\circ\text{C}$, 2.0 wt. % catalyst, reaction time of 64 h, 10 % TRI in DCM).

Synergy between Brønsted and Lewis acid sites for OME synthesis from TRI and OME_1

In order to get a better insight into the nature of this synergistic effect, reaction R1 was performed with higher time resolution with H-Beta-P, 2-DeAl and the partially dealuminated, Sn-modified samples (Fig. 7a). All catalysts exhibited a transition period in the beginning of the reaction due to an equilibration of temperature between the reactor and the thermostated bath. This resulted in an acceleration of the reaction rate observed for all catalysts during the first five minutes of the reaction. H-Beta-P first reached the maximal TRI conversion, closely followed by the zeolites containing both Brønsted and Lewis acid sites. However, the turnover frequency (TOF) was the lowest over H-Beta-P, followed by 2-DeAl (Fig. 7a, inset). The higher TOF value obtained with 2-DeAl compared to H-Beta-P could be due to a combination of two factors. First, dealuminated zeolites have stronger acid sites (higher Si/Al), which could accelerate the catalytic cycle due to reduced values of activation energy.^[39] Second, the dealumination treatment could have removed possible Al-rich debris present in the parent zeolite framework, thereby lowering the risk of OME internal molecular diffusion limitation.^[13] Compared to 2-DeAl and H-Beta-P, a two- and four-fold increase of the TOFs was observed obtained for 0.5Sn-2-DeAl, respectively, which we explain with the synergistic effect of Brønsted and Lewis acid sites. However, addition of Sn beyond the concentration in 0.5Sn-2DeAl resulted in a decrease of the TOFs. Such trend was already reported for the Sn-Beta in other catalytic reactions and means that not each Sn species is active for OME synthesis.^[40,41]

MF is a by-product of OME synthesis and results from the condensation of two formaldehyde units.^[2] MF production was notably higher for H-Beta-P, while partial dealumination suppressed MF production to values below the detection limit (Fig. 7b). This phenomenon is probably due to the reduced acid site

density and the resulting increased distance between two Brønsted sites in the zeolite framework obtained in 2-DeAl.^[9]

Fig. 7. Synthesis of OME using various catalysts from OME₁ and TRI concentration ($T = 30\text{ }^{\circ}\text{C}$, 0.5 wt. % catalyst, molar ratio OME₁:TRI = 3.3). (a) TRI conversion X_{TRI} vs. time and (inset) max TOF. The experimental data were fitted using the Boltzmann model and the maximum rate of reaction is calculated in Fig. S6. (b) Methyl formate production vs. time.

When the average distance between two Brønsted sites exceeds the distance, which is required for condensation of two formaldehyde units, MF formation is no longer possible. Lewis acid sites were also producing MF, proportionally to the Sn loading (Fig. 7b, inset). However, their activity was much lower compared to Brønsted sites. After 30 minutes, 10Sn-2-DeAl produced $0.39\text{ mmol}\cdot\text{L}^{-1}$ of MF compared to $14.02\text{ mmol}\cdot\text{L}^{-1}$ for H-Beta-P.

Analysis of other reaction parameters provided additional evidence on the nature of the synergistic effect. First, all samples displayed a linear relationship between the concentration of OME₂₋₈ and TRI conversion (Fig. 8a) with only small amounts of the intermediate FA found in the reaction mixture. This suggests that TRI decomposition to formaldehyde was the rate determining step. This interpretation is in accordance with previous studies that have identified decomposition of the FA source as the rate limiting step and its large energy barrier (between $60\text{--}80\text{ kJ}\cdot\text{mol}^{-1}$).^[19,21,25,42] Additionally, FA concentration only increased during the reaction for all catalysts and reached a stable level once a SF distribution of OME was reached (Fig. S7a), suggesting that FA insertion is not the rate limiting step of the reaction.

Furthermore, it challenges the possibility that tetrahedral Sn assists with the decomposition of TRI into formaldehyde units. A higher TRI conversion for a specific concentration of product should have been observed if tetrahedral Sn had been active in TRI decomposition, and this effect should have increased with increasing Sn content, which was not observed. FA concentration as a function of TRI conversion was also independent of the various catalysts, which means that TRI conversion reflects the reaction progress (Fig. S7b).

This was further confirmed by the analysis of the intermediate-to-product ratio (FA/OME₂₋₈) as a function of TRI conversion (Fig. 8b). Catalysts containing only Brønsted acid sites and catalysts containing both Lewis and Brønsted acid sites displayed a similar pattern, which suggests that FA concentration during the reaction was a function of the reaction progress and was not influenced by the presence of Lewis acid sites.

TRI insertion into OME₁ to form OME₄ was observed in the beginning of the reaction (Fig. S8). However, this phenomenon was not promoted by using dealuminated, Sn-containing zeolites. Therefore, the possibility that Lewis acid sites assist TRI insertion in OME₁ was ruled out.

Fig. 8. Synthesis of OME using various catalysts from OME₁ and TRI concentration (T = 30 °C, 0.5 wt. % catalyst, molar ratio OME₁:TRI = 3.3); (a) OME₂₋₈ concentration vs. TRI conversion X_{TRI} and (b) intermediate to product ratio vs. TRI conversion X_{TRI} .

Discussion

Catalyst characterization demonstrated that tetrahedrally coordinated Sn was successfully incorporated in the framework of the dealuminated zeolites. The partially dealuminated, Sn-grafted samples presented both Brønsted and Lewis acid sites, while H-Beta-P and 2-DeAl exhibited Brønsted acid sites and 50Sn-14-DeAl only Lewis acid sites. It has to be mentioned that H-Beta-P might contain residual Lewis acidity below the detection limit due to extra-framework Al. For 50Sn-14-DeAl, ICP-OES indicated residual aluminum, which is a potential source of Brønsted acidity. However, pyridine adsorption spectroscopy did not show any sign of Brønsted acidity for this sample and only Lewis acidity could be found. We conclude from these findings that the potential residual Lewis acidity in H-Beta-P and Brønsted acidity in 50Sn-14-DeAl can be neglected in the interpretation of the results. Please note that due to the low concentration of Sn in 0.5Sn-2-DeAl, some characterization methods such as MAS-NMR could not provide enough signal and the state of Sn was thus interpreted using samples with a larger Sn concentration.

These catalysts were used in a series of reactions to clarify the role of Lewis and Brønsted acid sites in the various synthesis steps (Table 2). Strong Brønsted acid sites, resulting from bridging hydroxyl groups, were active in all OME synthesis steps (i.e. initiation, growth and termination), independent of the reactants. Dealumination decreased the concentration of Brønsted acid sites, leading to an almost proportional reduction of the catalyst performance. In comparison, Lewis acid sites resulting from tetrahedrally coordinated Sn incorporated in the zeolite framework were not active in all steps involved in OME synthesis. First, Lewis acid sites could not catalyze the OME initiation/termination step. Second, they could not decompose TRI into FA units, while they could decompose PF. However, a synergy between Brønsted and Lewis acidity was observed for the reaction of OME₁ with TRI or PF. Notably, production of OME

from OME₁ and TRI using 0.5Sn-14DeAl resulted in a four-fold increase in TOF compared to H-Beta. No synergy was detected when producing OME from MeOH and FA.

The first difference in activity between Lewis and Brønsted acid sites was observed during the initiation-termination step, which, unlike Brønsted acid sites, did not occur on Lewis acid sites. On the one hand, OME₂ equilibration experiments demonstrated that addition of Sn was detrimental to the catalyst performance, showing the inability of Lewis acid sites to activate OME₂ through generation of a carbocation. On the other hand, tetrahedral Sn-catalyzed OME synthesis from FA and MeOH demonstrated the activity of the Sn sites for acetalization. The activity of 50Sn-14DeAl in R2 is probably due to the generation of water from the decomposition of PF, which should be sufficient to reverse acetalization.

The second difference in activity is related to TRI decomposition into FA units, which did not occur on tetrahedrally coordinated Sn. 50Sn-14-DeAl exhibited an activity superior to 14-DeAl for R2, while both catalysts were inactive for R1.

Table 2. Activity comparison of Brønsted and Lewis acid sites for the various OME synthesis steps.

Synthesis Steps	Reactant /intermediate	Brønsted (bridging hydroxyl)	Lewis (tetrahedral Sn)
Initiation/Termination	Carbocations	Active	Inactive
	Hemiformal	Active	Active
Growth/Sequential addition		Active	Active
Decomposition of FA source	TRI	Active	Inactive
	PF	Active	Active

Thus, PF must have been decomposed on Lewis acid sites into FA units, which were subsequently used for OME growth. However, it appeared that the activity of tetrahedrally coordinated Sn for PF decomposition was not as high as Brønsted acid sites. Meanwhile, TRI decomposition in DCM revealed that TRI conversion was due to the presence of Brønsted acid sites and that addition of low to moderate Sn concentration did not improve TRI conversion. Additionally, detailed investigation into R1 revealed that, despite their very different activity, the intermediate-to-product ratio did not vary during the course of the reaction among the catalysts (i.e. H-Beta-P, 2-DeAl, and partially dealuminated, Sn-modified samples). The possibility that TRI was inserted into OME₁ was also discarded based on the comparison of OME₄ production versus OME₂₋₈.

The synergy between Brønsted and Lewis acidity, which resulted in a four-fold increase in TOF, was only observed for reactions involving OME₁ and a FA source (i.e. R1 and R2). No synergy was detected when OME were produced from MeOH and FA. This is in accordance with the results of Li et al., showing no synergy between Brønsted and Lewis acid sites for the reaction of MeOH with TRI.^[22] It is important to note, from our results and previous studies, that such a synergy was only reported when OME₁ was used as one of the reactants.^[22,26] The presence of water could also be an important factor to obtain such a synergy. When using MeOH or formalin, water from the reaction medium or produced during acetalization could coordinate with Lewis acid sites to convert them to Brønsted acid sites. That could potentially explain why no synergy was observed under these conditions. The effect of water on the reaction kinetics of OME synthesis from TRI and OME₁ is currently investigated and subject of a separate study.

Because tetrahedral Sn was not active for TRI decomposition and OME initiation to carbocations, the synergy between Brønsted and Lewis acid sites can only be explained by a higher activity of tetrahedral Sn in the OME growth step. FA units were made available by TRI decomposition on Brønsted acid sites and growth occurred on tetrahedral Sn as Lewis acid sites, which increased the overall reaction rate. Increasing the Sn concentration further in the partially dealuminated zeolite decreased the TOF, but

presence of a small amount of Lewis acid sites may have been sufficient to rapidly incorporate the produced FA into OME.

Activation of the carbonyl group of FA by interaction with tetrahedral Sn could likely be the initial step for insertion of FA into OME. This finding was supported by results from TRI decomposition in DCM, which showed an increase in MF production with an increasing Sn content, which probably is a result of FA activation by Sn. Furthermore, dealuminated, Sn-modified catalysts also produced much less MF compared to H-Beta-P during OME synthesis, which suggests that FA units were rapidly inserted in OME. Thus, we suggest that the synergy between Brønsted and Lewis acid sites is a consequence of TRI dissociation on Brønsted acid sites and sequential addition on Lewis acid sites, as illustrated in Scheme 4.

Conclusions

In summary, tetrahedrally coordinated Sn was successfully incorporated in the framework of dealuminated BEA zeolites via Sn grafting in dichloromethane leading to a series of BEA zeolites with varying Lewis and Brønsted acid sites. The synthesized catalysts were used for a combination of OME synthesis reactions to clarify the role of Brønsted and Lewis acid sites. Our results demonstrated that Lewis acid sites resulting from tetrahedrally coordinated Sn were not active in all OME synthesis steps, while Brønsted acid sites were. Notably, TRI dissociation and OME₁ activation did not occur on Lewis acid sites. The presence of both sites resulted in a synergy when OME₁ was used with PF or TRI. Notably, 0.5Sn-2-Deal exhibited a significant increase in TOF and reduction in byproduct generation. This synergistic effect was explained by a more efficient FA insertion into OME on Lewis acid sites, while production of FA units by TRI or PF decomposition occurred on Brønsted acid sites. The interaction between tetrahedral Sn and the carbonyl group of FA resulted in an activated FA, likely to be inserted into OME.

Scheme 4. Suggested reaction mechanism for the synthesis of OME from OME₁ and TRI with Brønsted and Lewis sites. Reaction with OME₁ was depicted for readability.

Experimental Section

Partial and complete dealumination of zeolite Beta

Partial or complete dealumination were performed on a Beta zeolite (Si/Al = 11, ABCR). The parent H-Beta zeolite (H-Beta-P) was first obtained by calcination of NH_4 -Beta at 550 °C for 5 h with a 10 °C·min⁻¹ temperature ramp. Partial dealumination was achieved by stirring the zeolite overnight in a 2.0 M solution of nitric acid (HNO_3 , 65 %, Sigma Aldrich) at 80 °C under reflux (55 mL·g⁻¹ catalyst). Alternatively, a solution of 14.0 M HNO_3 (50 mL·g⁻¹ catalyst) stirred at 100 °C under reflux for 8 h was used for complete dealumination. The partially or completely dealuminated zeolite was then filtered and repeatedly washed with deionized water until a neutral pH was reached. The powder was then dried overnight in an oven at 110 °C. The partially and completely dealuminated zeolites were named 2-DeAl and 14-DeAl, respectively, according to the HNO_3 concentration used during the treatment.

Post-synthetic Sn grafting of dealuminated Beta zeolite in dichloromethane

Dealuminated Beta zeolite (2-DeAl or 14-DeAl) was first thoroughly dried under vacuum at 200 °C overnight. Anhydrous dichloromethane (DCM, 99.8 %, Acros) was added to the powder through moisture-free cannula transfer (100 mL·g⁻¹ catalyst) using Schlenk technique. A determined amount of SnCl_4 (1.0 M in DCM, Acros) was subsequently added with a syringe and the mixture was stirred magnetically (450 rpm) at 70 °C for 7 h under reflux in N_2 .^[27] The powder was then recovered by filtration and thoroughly washed with dry isopropanol (Acros). Next, the recovered solid was dried at 110 °C overnight and calcined at 550 °C for 5 h under static air with a temperature ramp of 10 °C·min⁻¹. Each catalyst is denoted as xSn-y-DeAl, where x and y are the Sn precursor concentration and the HNO_3 concentration during dealumination, respectively.

Material Characterization

N_2 physisorption experiments were performed on a Micrometrics 3Flex apparatus at 77 K and N_2 relative pressures between 10⁻⁵ and 0.99. Typically, samples (ca. 150 mg) were dried at 120 °C (temperature ramp 5 °C·min⁻¹) for 5 h. A leak test was performed before the analysis. Brunauer-Emmett-Teller (BET) surface, Barrett-Joyner-Helenda (BJH)

and t-plot method were used, respectively, to calculate the specific surface area, the mesoporous, and microporous volume. Elemental analyses were performed using inductively coupled plasma optical emission spectrometry (ICP-OES) at the Paul Scherrer Institute on a Vista pro AX Varian instrument. A 10 mL aqueous solution containing 0.5 mL of 65% nitric acid, 0.5 mL of 40% hydrofluoric acid and 0.25 mL of 30% hydrochloric acid was used for the digestion of 50 mg of catalyst at 95 °C for 2 h.

XPS spectra were recorded using a monochromatic Al K α X-ray source of 24.8 W and a beam size of 100 μm on a PHI VersaProbe II scanning XPS microprobe (Physical Instruments AG, Germany). X-ray diffraction (XRD) patterns were recorded using a D8 advance Bruker instrument equipped with a 1D-LynxEye detector (Cu K α radiation, no monochromator, Ni filter) at a step size of 0.01°. The structure of the samples was studied by high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) on a FEI Tecnai Osiris with 200 kV acceleration voltage. The energy-dispersive X-ray spectroscopy results were analyzed using Bruker Esprit Software. Grids were prepared by deposition of a drop of ethanol containing the sample on a Lacey carbon grid.

Magic angle spinning nuclear magnetic resonance (MAS-NMR) was used to investigate the coordination and chemical environment of Sn. ¹¹⁹Sn single-pulse spectra were collected on a 500 MHz Bruker instrument equipped with a 11.7 T magnet, at room temperature with a 35 kHz spinning rate. The Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence was performed to increase the sensitivity, on a 900 MHz Bruker Avance instrument.

Concentration of acid sites was calculated from temperature programmed desorption of NH_3 (NH_3 -TPD) on a Micromeritics Autochem 2920 II instrument. Typically, the sample (ca. 100 mg) was loaded in a quartz cell and dried with a He flow (50 mL·min⁻¹) at 200 °C (2 °C·min⁻¹; hold time of 120 min). Saturation of the sample with NH_3 was done using a volumetric ratio of 1:99 for NH_3 and He during 1 h at 50 °C. Physisorbed NH_3 was then removed with He (50 mL·min⁻¹). The temperature was then increased to 600 °C (10 °C·min⁻¹) and NH_3 was monitored using a calibrated MKS Cirrus II mass spectrometer.

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was performed by means of a high temperature Harrick DRIFT cell mounted on a Perkin Elmer Frontier spectrometer equipped with a mercury cadmium telluride detector. Spectra were recorded with 32 scans at a resolution of 4 cm⁻¹ after being dried 2 h at 200 °C under a 20 mL·min⁻¹ He flow. Pyridine adsorption experiments were done using the following procedure. First, the

sample was dried and consequently saturated at 50 °C for 30 min under a He flow of 20 mL·min⁻¹ bubbling through pyridine at room temperature. Physisorbed pyridine was then removed by flowing pure He (20 mL·min⁻¹) for 30 min. Finally, the temperature was raised to 150 and 300 °C with a ramp rate of 5 °C min⁻¹. Diffuse reflectance UV-Vis spectroscopy (DRUVS) spectra were recorded on a Varian spectrometer equipped with an in-situ Harrick Praying Mantis cell. In-situ measurements were done under a N₂ flow of ca. 20 mL·min⁻¹.

Catalytic testing for OME synthesis

TRI (99 %) and PF were purchased from Sigma-Aldrich. OME₁ (99.5 %) was obtained from Acros and OME₂ to OME₆ (99.0 %) were purchased from ASG Analytics. The H₂O content of OME₁ was determined by Karl-Fisher titration (0.04 wt. % H₂O). A methanolic formaldehyde solution was prepared from PF and MeOH. PF was dissolved in MeOH and heated overnight at 60 °C under magnetic stirring with the addition of a few drops of base (sodium methoxide). Undissolved PF was removed by filtration.

Synthesis of OME was performed in 10 mL pressure resistant glass reactors (Grace GmbH). Typically, the reactors were loaded with catalysts and dried overnight at 110 °C. After cooling down to RT, the reactants were added and the reactors were subsequently dipped in a water bath thermostated at the reaction temperature, which was considered as the start of the reaction. The reaction mixtures were stirred magnetically at 400 rpm and were quenched in ice at a determined time. Samples were filtered before analysis and formaldehyde titration. TRI decomposition in dichloromethane (DCM) was performed using a similar method, using a 10 wt. % TRI solution of DCM, previously dried over molecular sieve. Reactors were loaded with 2 wt. % catalyst, relative to TRI.

Analysis of the samples was performed on an Agilent 7890B/5977A series gas chromatograph-mass spectrometer (GC-MS) with an automated liquid sampler and an HP-5 capillary column (length 30 m, outer diameter 0.32 mm, film 1.05 µm). Quantification of OME₁₋₆, methanol and methyl formate was done by means of a calibration curve that was obtained with pure reference materials. Calibration curves for OME₇₋₈ were constructed based on the effective carbon number method and extrapolated from the response factors of OME₁₋₆.^[43] Formaldehyde concentration was determined by 3 successive titrations using the sodium sulfite method.

Experimental data from R1 were fitted with the Boltzmann function using the ORIGIN software. The turnover frequencies (TOFs) were calculated using the following formula:

$$TOF_{max} = \frac{rate_{max}}{C_{ac} \cdot C_{cat}}$$

where rate_{max} is the maximum value of the derivative of [OME₂₋₈] vs. time (mol·L⁻¹·s⁻¹), C_{ac} is the acid sites concentration of the catalyst (mol·g⁻¹) and C_{cat} is the catalyst concentration (g·L⁻¹).

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FULL PAPER

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Sn grafting on a dealuminated zeolite Beta resulted in a catalyst with both Brønsted and Lewis acidity, which was used for OME synthesis. The synergy of both acid sites resulted in a four-fold increase in turnover frequency and a reduction of by-product generation. The nature of the synergy is due to the interaction between Sn and formaldehyde.

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Nature of the synergy between Brønsted and Lewis acid sites in Sn-Beta zeolites for polyoxymethylene dimethyl ethers synthesis