Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Formaldehyde-isobutene Prins condensation over MFI-type zeolites

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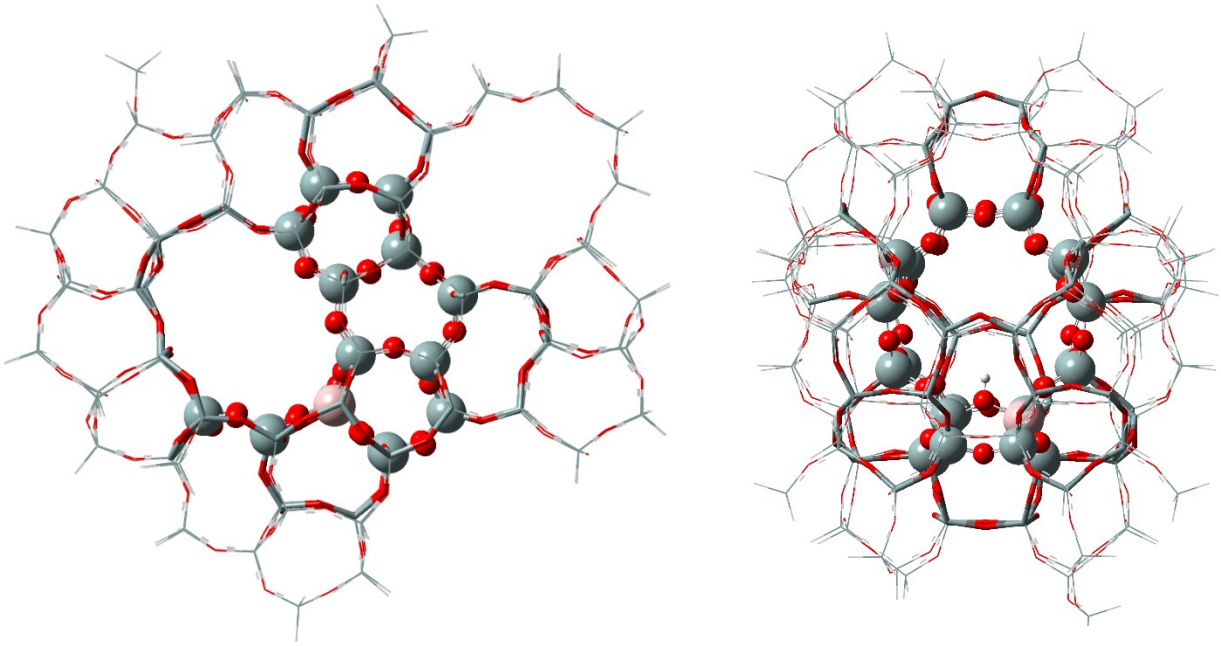


Figure S1. Two views of the H-ZSM5 ONIOM model. High-theory layer shown in ball-and-stick representation, intermediate theory in tube representation and low-theory layer in wireframe representation. Color codes: Pink, Al; red, O; gray, Si; and white, H.

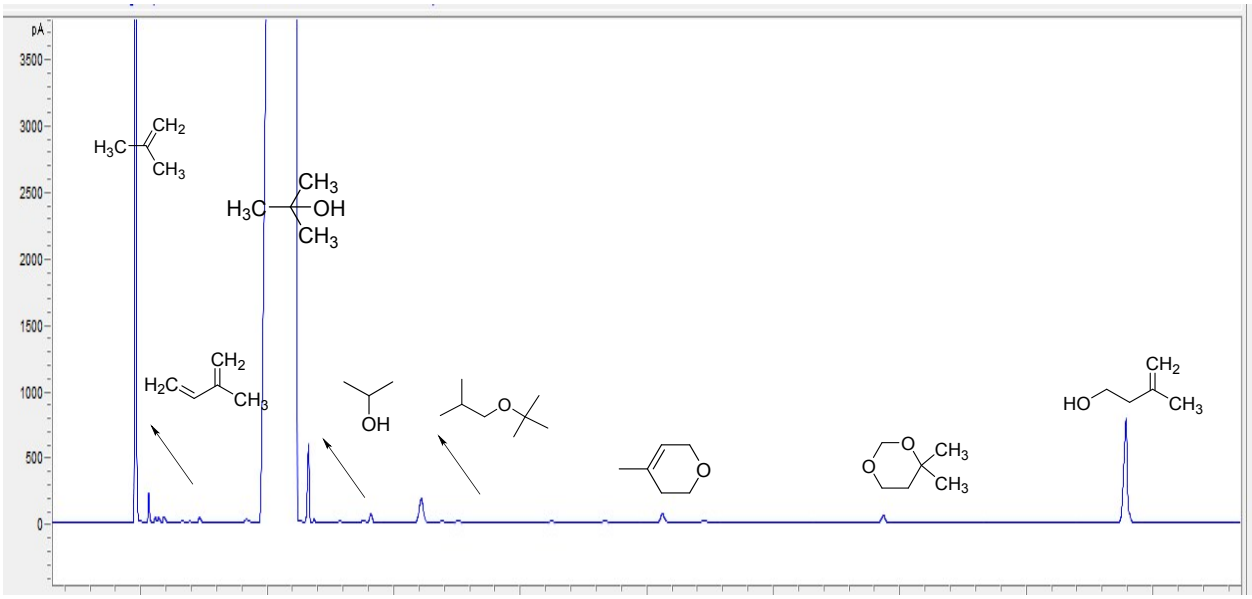
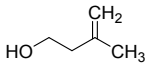
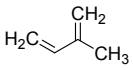
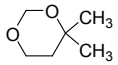
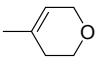


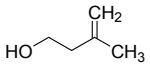
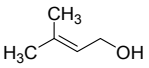
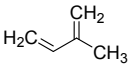
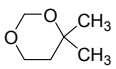
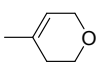
Figure S2 GC chromatograph of the liquid product obtained after t-butanol and formaldehyde reaction, H-ZSM-5(40), T=423K, t_r=1h, $C_4H_{10}O/CH_2O$ molar ratio=77.5, 2-propanol is contained in t-butanol

Table S1 Effect of C_4H_8/CH_2O molar ratio on product selectivity for the isobutene and formaldehyde reaction

C_4H_8/CH_2O molar	Carbon-based Selectivity (%)			
				
1.60	54.5	18.5	8.6	16.5
3.15	27.3	54.5	3.6	13.6
6.30	30.7	57.7	2.5	9.1

T=423K, t_r=1h, H-ZSM-5(40), catalyst amount=0.25g

Table S2 Effect of reaction temperature on CH_2O conversion and selectivity for the isobutene and formaldehyde reaction

Temperature (K)	CH_2O Conversion (%)	Carbon-based Selectivity (%)				
						
323	24.3	90.8	4.9	1.7	0.0	2.6
348	44.3	87.1	5.8	2.2	0.0	4.7
373	53.8	81.3	2.7	6.7	3.2	6.2
398	49.9	64.4	1.9	21.2	2.9	9.5
423	44.3	27.3	1.1	54.5	3.6	13.6
453	48.5	4.5	3.1	74.2	2.9	15.2

t_r=1h, C_4H_8/CH_2O molar ratio=3.15, H-ZSM-5(40), catalyst amount=0.25g

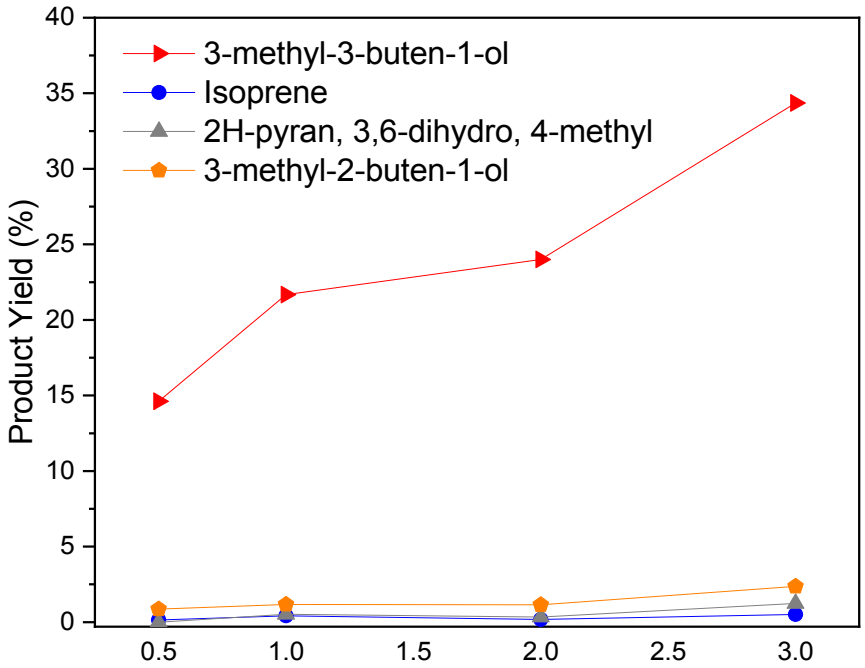


Figure S3 Product Yield versus reaction time, T=323K, C_4H_8/CH_2O molar ratio=3.15, catalyst amount=0.25g

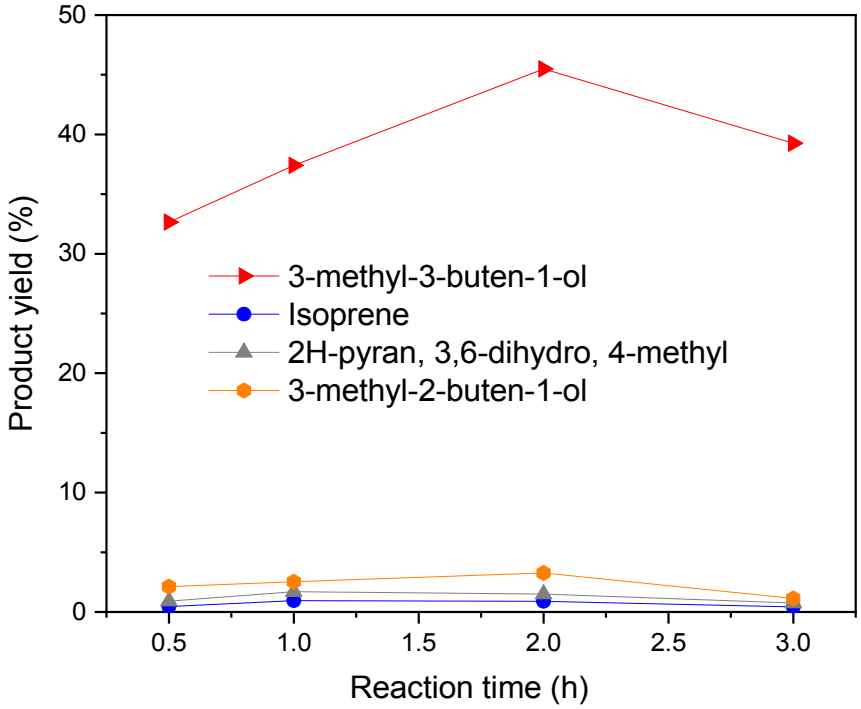
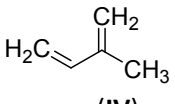
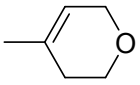


Figure S4 Product Yield versus reaction time, T=348K, C_4H_8/CH_2O molar ratio=3.15, catalyst amount=0.25g

Table S3 Effect of temperature on 3-methyl-3-buten-1-ol reactivity

Temperature (K)	**I** Conversion (%)	Carbon-based Selectivity (%)	
		 (**IV**)	 (**V**)

323	0.4	100.0	0.0
373	70.1	82.1	17.9
398	89.0	75.7	19.7
423	100.0	94.0	6.0

t_r=1h, catalyst/$C_5H_{10}O$ wt=3.7, H-ZSM-5(40), catalyst amount=0.25g

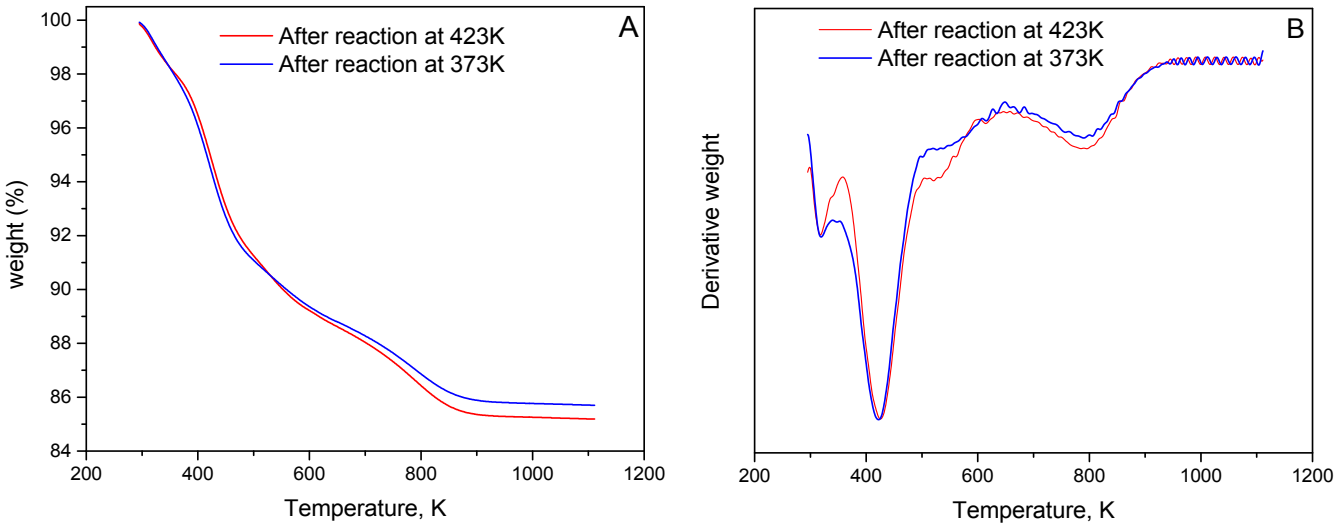


Figure S5 A: Actual and B: derivative weight versus temperature, Analysis conditions: air flow=50ml/min, rate=10o/min, temperature=room temperature to 1100K, Reaction conditions: Temperature=373 and 423K, tr=1h, C_4H_8/CH_2O molar ratio=3.15, catalyst amount=0.25g

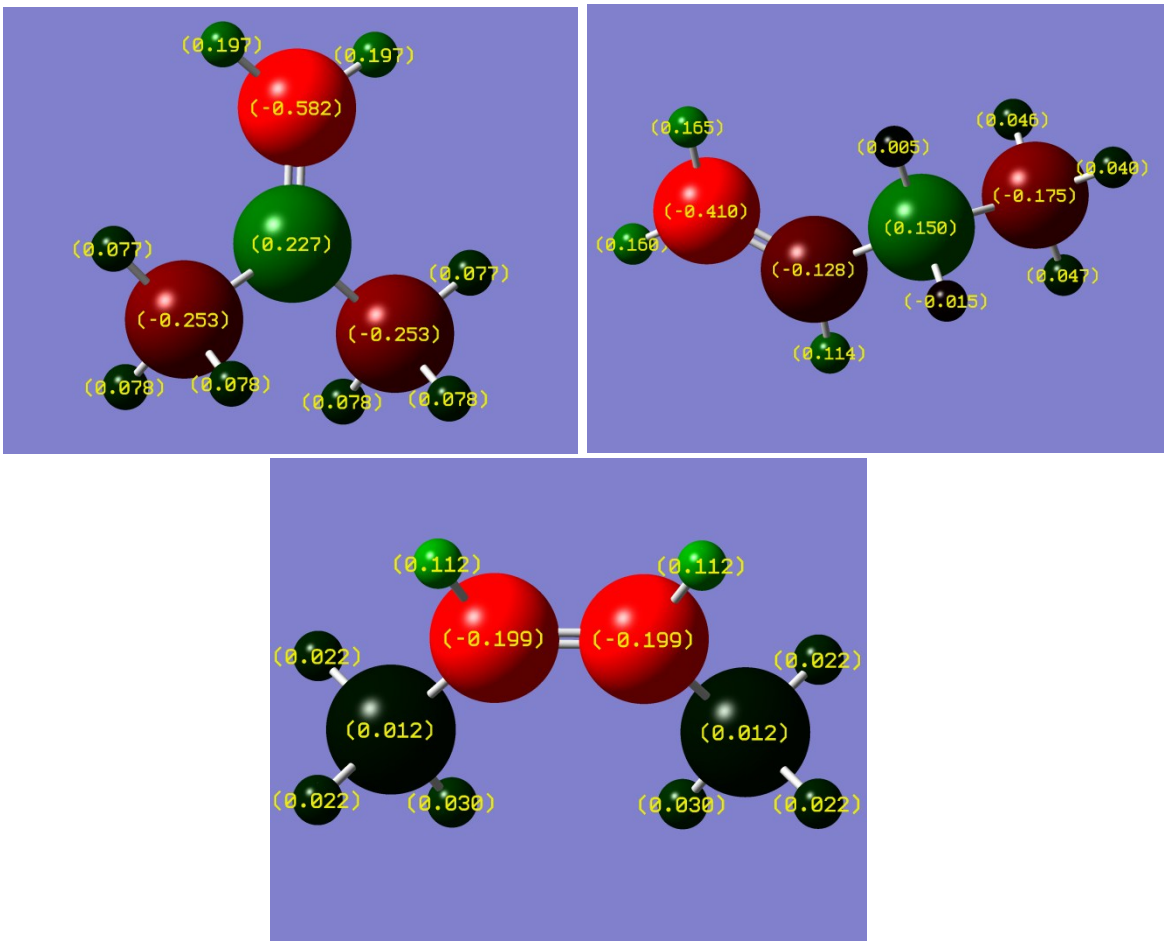


Figure S6 Clockwise, partial charges on isobutene, 1-butene and cis-2-butene calculated by fitting to the electrostatic potential (CHELPG).[1]

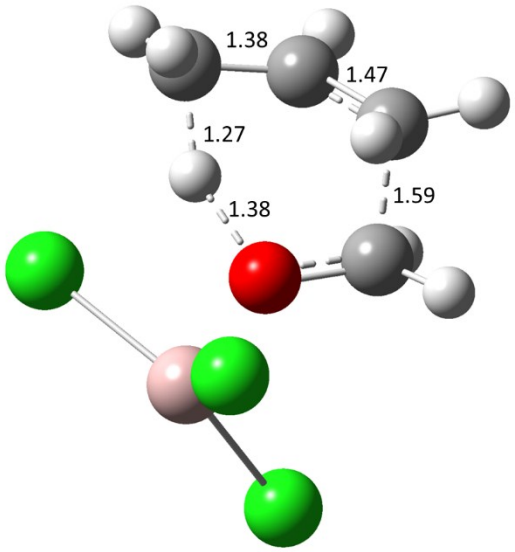


Figure S7 Transition state structure of the carbonyl-ene reaction of formaldehyde with propene catalyzed over Lewis acid $AlCl_3$. Bond lengths are given in Å. (Reproduced from data provided in Fig. 3. of Ref 40).

References

1. C. M. Breneman and K. B. Wiberg, *J. Comput. Chem.* 1990, **11**, 361-373