

Kinetics, Mechanism and Site Requirements for Dimethyl Ether Carbonylation on Acidic Zeolites

Aditya Bhan¹, Patricia Cheung¹, Ayman Allian¹, Glenn Sunley², David Law², and Enrique Iglesia^{1*}

¹University of California, Berkeley, CA 94720 (USA)

²BP Chemicals, Hull Research and Technology Center, Saltend, Hull HU128DS (UK)

*iglesia@berkeley.edu

Methanol carbonylation using homogeneous Ir/ Rh noble metal catalysts and iodide co-catalysts represents the current industrial practice for producing acetic acid [1]. We report here the selective (>99%), low-temperature (408-453 K) carbonylation of dimethyl ether (DME) to produce methyl acetate, a precursor to acetic acid, on acidic zeolites, without detectable catalyst deactivation or the requirement for halide co-catalysts.

Carbonylation rates (per Al; 20 kPa DME, 930 kPa CO, 50 kPa Ar; 438 K) depend strongly on zeolite structure, with H-MOR [0.9 mol (g-atom Al h)⁻¹] and H-FER [0.1 mol (g-atom Al h)⁻¹] showing much higher rates than H-MFI, H-BEA, or USY. Steady-state kinetic studies on H-MOR (Si/Al =10, Zeolyst) showed that carbonylation rates were independent of DME pressure (0.8 - 8.0 kPa) and proportional to CO pressure (0-930 kPa). These kinetic data indicate that (i) active sites are saturated with DME-derived intermediates, (ii) CO addition is the kinetically-relevant step, and (iii) CO and DME do not compete for the same binding centers. The addition of water (0.5-1.1 kPa) to DME-CO reactants led to a 10-fold decrease in methyl acetate synthesis rates without concurrent formation of acetic acid. This inhibition by H₂O was reversible. It does not reflect competitive adsorption of H₂O with DME or the displacement of DME-derived intermediates, because rates remain zero-order with respect to DME, even in presence of H₂O [2].

An uptake of 0.5±0.05 DME/Al was observed on different zeolite types (H-MFI, H-MOR, H-FER) upon exposure to DME pulses at 423 K, irrespective of the amount of DME added (DME/Al added = 0.73-1.00). These data indicate that DME reacts with Brønsted acid sites in zeolites to form water and methyl groups. *In situ* infrared spectroscopy during DME reactions (DME/Al = 1.2 cumulative, H-MOR Si/Al=10) showed a sharp decrease in the intensity of acidic O-H stretches (~3600 cm⁻¹) upon DME addition, and a concurrent increase in the intensity of the bands at 2978 and 2868 cm⁻¹, for antisymmetric and symmetric C-H stretches in methyl groups; these bands persisted during evacuation at 423 K for 1 h, consistent with the presence and stability of CH₃ groups at zeolitic exchange sites. The abrupt replacement of DME-CO mixtures with pure CO for varying time intervals led to the formation of methyl acetate precursors, which desorbed, however, only after pure DME or DME-CO reactants were re-introduced. Subtracting steady-state rates from "excess" methyl acetate formation rates and integrating over time in DME-CO reactants allowed measurements of the number of excess methyl acetate molecules formed (per Al) during previous exposure of pre-formed methyl groups to CO(g). These excess amounts reflect, in turn, the number of stranded acetyl species formed upon reactions of CO with surface CH₃ groups, which increased monotonically with increasing time of exposure to CO(g). These acetyls desorb (as methyl acetate) upon their rapid

methoxylation by DME in a step that restores the methyl group consumed to form acetyl groups and completes a catalytic cycle that maintains anhydrous conditions during steady-state carbonylation (Figure 1). The initial rate of CO-CH₃ reactions calculated from the number of excess methyl acetate per Al formed during transient experiments are ~ 2 times lower than for steady-state carbonylation for H-MOR and H-FER. The good agreement between transient and steady-state rates and the lack of kinetic isotope effects measured using CH₃OCH₃-CO and CD₃OCD₃-CO mixtures (k_H/k_D = 1.06) at 438 K on H-MOR, leads us to conclude that formation of C-C bonds via CO insertion into O-CH₃ bonds is the sole kinetically-relevant step in DME carbonylation [2,3].

Studies of H-MOR samples with different Brønsted acid site concentrations (by changing Na/Al or Si/Al) show that methyl acetate synthesis rates (per available H⁺) increased monotonically with increasing H⁺ concentration. These trends are inconsistent with the sole involvement of H⁺ species of uniform reactivity in stabilizing intermediates required for kinetically-relevant CH₃-CO reactions. It appears that reactivity of methyl or oxonium groups on H⁺ sites depends on the number and identity of vicinal sites or on the specific location of these sites within channels or side pockets. The identity of CO-derived species that non-competitively adsorb with DME remains equivocal at this time. Carbonylation rates however, did not vary monotonically with the number of CO binding Lewis acid sites measured by ²⁷Al MAS NMR, infrared spectra of CO adsorbed at low temperatures, or CO desorption studies, suggesting that CO strongly bound on Lewis acid sites (<5% of Al sites) is not involved in carbonylation reactions. The linear dependence of rates on CO pressures (up to 1 MPa) indicates that any CO-species bound strongly enough to be detectable in spectroscopic studies does not correspond to the kinetically-relevant CO-derived reactive intermediate. In context of these results and of on-going theoretical studies, we will discuss the site requirements for DME carbonylation, specifically for steps leading to the formation of the C-C bond during DME carbonylation to methyl acetate [4].

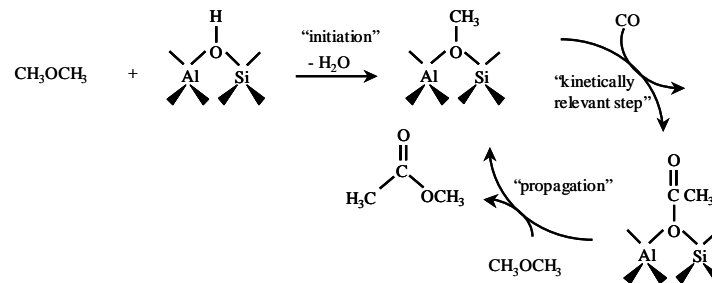


Figure 1. Proposed sequence of elementary steps for DME carbonylation [2,3].

References

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