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Acid strength and metal-acid proximity effects on methylcyclohexane ring contraction turnover rates and selectivities

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ABSTRACT

Methylcyclohexane ring contraction is used here to assess the effects of acid strength and metal-acid site proximity on turnover rates and selectivities for bifunctional catalysts consisting of Keggin type polyoxometalates (POM) with different central atoms that act as Brønsted acids. Bifunctional catalysts with metal sites that fully equilibrate cycloalkanes and cycloalkenes give methylcyclohexene conversion rate constants that decreased exponentially with increasing deprotonation energy, a rigorous descriptor of acid strength, consistent with the ion-pair character of transition states that mediate the kinetically-relevant ring contraction of bound methylcyclohexoxide intermediates. The measured rates of formation of each alkylcyclopentane isomer, however, do not reflect their intrinsic formation kinetics, because of fast diffusion-enhanced interconversions within acid domains; thus, isomer selectivities cannot be used to infer, even indirectly, the strength of acid sites, as often proposed in previous studies. Selectivities reflect instead diffusional effects that become more severe as the number and strength of acid sites and the size and diffusive resistances increase within these acid domains, which shift, in turn, the products formed from relative abundances dictated by kinetics to those prescribed by thermodynamics. A rigorous accounting of these diffusional effects using a kinetic-transport model leads to ratios of intrinsic rate constants for the formation of the different alkylcyclopentane isomers that do not depend on acid strength, because all isomerization routes are mediated by bicyclo[3.1.0]hexyl cation transition states similar in the amount and location of charge and that therefore benefit to the same extent from the more stable conjugate anions characteristic of stronger acids.

1. Introduction

The contraction of methylcyclohexane rings to form alkylcyclopentanes on bifunctional catalysts consisting of Brønsted acid and metal functions is often used as a probe of acid strength and of the effects of confinement within amorphous and crystalline solid acids [1–4], and it is also of industrial importance because such chemistry is paramount for the effective conversion of ethylbenzene to xylene isomers [5,6]. Yet, connections between reactivity, selectivity, and acid strength remain empirical because of the challenges inherent in assessing the number and strength of acid sites and their consequential distances from the metal function, and the identity and reversibility of the elementary steps that mediate such reactions. These hurdles are overcome here by using Brønsted acids with known structure and acid strength, measuring acid site densities during catalysis, dispersing a metal function that maintains cycloalkane-cycloalkene equilibria, and rigorous mechanistic interpretation of measured rates and selectivities.

Tungsten polyoxometalate (POM) clusters with Keggin structures and charge-balancing protons ($H_{8-n}X^{n+}W_{12}O_{40}$) are Brønsted acids with uniform and well-defined atomic connectivity and diverse chemical composition ($X^{n+} = P^{5+}, Si^{4+}, Al^{3+}, Co^{2+}$) [7]. Their acid strength and the reactivity of their protons depend on their central atoms, because of their concomitant effects on the number of protons and on the stability of the conjugate anion [8]. Deprotonation energies (DPE) reflect the energy required for heterolytic cleavage of a proton from the conjugate base, thus providing a rigorous measure of acid strength accessible to calculation by density functional theory (DFT) for solids with known structures, such as Keggin POM clusters (1087–1143 kJ mol^{-1} for $H_{8-n}X^{n+}W_{12}O_{40}$; X = P, Si, Al, or Co in order of increasing DPE) [8,9].

Our recent studies have shown that first-order rate constants for the isomerization of acyclic alkenes [10] and for the dehydration of alkanols [7,11,12] (per accessible H$^+$) decrease exponentially with increasing DPE (decreasing acid strength) for Keggin POM clusters with different central atoms (P, Si, Al, Co); such

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trends reflect the stability of ion-pair transition states (TS), which benefits from more stable conjugate anions. The sensitivity of alkene isomerization rate constants to DPE is similar for different hexene isomer reactants [10], because the amount and location of the positive charge are similar among the transition states that mediate such reactions. Consequently, alkene isomerization selectivities are insensitive to acid strength, because they solely reflect the stability of the protonated gaseous analogs of each isomerization of TS. The isomerization selectivities observed, however, do not only reflect such intrinsic selectivities, because of the ubiquitous role of fast secondary alkene interconversions that occur locally within porous acid domains before alkenes convert to alkanes either via hydrogen transfer at acid sites or via reactions with H_2 at metal sites in bifunctional catalysts [10].

Here, ring contraction rate constants (per H^+) for methylcyclohexane ring contraction are examined through mechanistic interpretations of rate and selectivity data combined with titrations of accessible protons during catalysis. Measured selectivities differ from their intrinsic values because of diffusion-enhanced interconversions among alkylcyclopentene products within acid domains. Such diffusional enhancements are stronger on catalysts with stronger and/or more abundant acid sites and in acid domains of larger size or smaller diffusion coefficients. Furthermore, experimental results indicate that rate constants for the formation of each primary alkylcyclopentane isomer increase exponentially with decreasing DPE values to the same extent, leading to intrinsic selectivities that do not depend on acid strength. These data show, once again, that ion-pair transition states of similar charge are affected similarly by the stability of the conjugate anion. Thus, measured selectivities (even at differential conversions) cannot be taken as evidence for acid strength [1,2,13,14]; the preferential formation of the products formed in more demanding isomerization routes does not reflect a concomitant preference for such reactions on stronger acids or in microporous acids. Instead, such trends arise from intrapellet gradients of product alkenes that become more severe on more reactive protons (stronger acids) or within porous media in which molecules diffuse more slowly or over greater distances. In the most severe cases, diffusion-enhanced interconversions move selectivities away from those determined by the relative rates at which primary isomer products are formed and toward their thermodynamic values.

2. Experimental methods

2.1. Catalyst preparation

Detailed catalyst synthesis procedures have been reported elsewhere [10]. $H_3PW_{12}O_{40}$ (Sigma-Aldrich; Reagent Grade; CAS #12501-23-4), $H_4SiW_{12}O_{40}$ (Aldrich; >99.9%; CAS #12027-43-9), $H_5AlW_{12}O_{40}$ (prepared according to [15]), and $H_6CoW_{12}O_{40}$ (prepared according to [16,17]) were supported on amorphous SiO_2 (Cab-O-Sil HS-5; 310 $m^2\ g^{-1}$; 1.5 $cm^3\ g^{-1}$ pore volume) at loadings of 0.04 and 0.20 POM $(nm^2\text{-}SiO_2)^{-1}$ using incipient wetness impregnation methods. SiO_2-supported POM clusters will be denoted herein as "H_nXW/SiO_2", where n is the proton stoichiometry. ^{31}P-MAS-NMR spectra showed that their dispersion onto the SiO_2 support and their use in catalysis retained the essential features of the NMR spectra of intact $H_3PW_{12}O_{40}$ Keggin structures [10]. Transmission electron micrographs showed that POM clusters are present as isolated clusters with a minority of two-dimensional aggregates at these POM surface densities (0.033–0.067 POM $(nm^2\text{-}SiO_2)^{-1}$) [10].

Pt/Al_2O_3 (1.5 wt% Pt) was prepared by incipient wetness impregnation of treated γ-Al_2O_3 (Sasol SBa-200; 193 $m^2\ g^{-1}$, 0.57 $cm^3\ g^{-1}$ pore volume; treated in dry air (UHP Praxair; 0.5 $cm^3\ g^{-1}\ s^{-1}$) at 923 K for 18 ks) with aqueous H_2PtCl_6 solutions (Aldrich; CAS #16941-12-1) [10]. The Pt dispersion (90%) was determined by H_2 chemisorption at 313 K (Quantasorb analyzer; Quantachrome Corp.) using a 1:1 H:Pt stoichiometry [10]. Pt/Al_2O_3 and H_nXW/SiO_2 (X = P, Si, Al, or Co) catalysts were mixed as intimate aggregates (<20 μm) using a mortar and pestle; these fine powders were pressed into wafers and then crushed and sieved to retain 125–180 μm aggregates. The composition of these mixtures is reported as the ratio of surface Pt-atoms (from H_2 chemisorption) to H^+ in POM clusters (from titrations with 2,6-di-*tert*-butylpyridine during catalysis; Section 2.2).

2.2. Ring contraction rate measurements and titrations of protons with 2,6-di-tert-butylpyridine during catalysis

Reaction rates and selectivities were measured on samples (0.040–0.103 g) packed within a stainless steel tubular reactor (3/8 in. O.D.) with plug-flow hydrodynamics. Reactor temperatures were measured with two K-type thermocouples (Omega; ±0.2 K), one held against the external reactor wall and the other held within a 1/16 in. stainless steel sheath aligned axially along the bed; temperatures were controlled using a resistively-heated furnace and PID control strategies (Watlow Series 982 controller). Transfer lines were kept at 423 K to prevent condensation of reactants, products, and titrants. A backpressure regulator was used to control pressure (Equilibar, model EB1LF2). Physical mixtures of Pt/Al_2O_3 and H_nXW/SiO_2 were treated in flowing H_2 (Praxair UHP) at 2 bar (0.16 $cm^3\ s^{-1}$ at STP) by heating to 473 K at 0.083 K s^{-1} and holding for 4 ks before catalytic measurements. Liquid methylcyclohexane (MCH; Sigma-Aldrich; >99%) was used without further purification and vaporized at 523 K into a flowing H_2 (UHP Praxair) stream using a liquid syringe pump (Cole-Palmer 74900 Series). Molar MCH and H_2 flow rates were set using electronic mass flow controllers to maintain a given (MCH/H_2) molar ratio and low MCH conversions (<10%).

Reactants and products in the reactor effluent were separated chromatographically (HP-1 column; 0.32 mm ID × 50 m, 1.05 μm film; Agilent) and detected using flame ionization (Agilent 6890 N GC). The predominant products detected were as follows: ethylcyclopentane (ECP), *cis*-1,3-dimethylcyclopentane (c13DMCP), *trans*-1,3-dimethylcyclopentane (t13DMCP), *trans*-1,2-dimethylcyclopentane (t12DMCP), 1,1-dimethylcyclopentane (11DMCP), several acyclic heptane isomers, and methylcyclopentane. *cis*-1,2-Dimethylcyclopentane (c12DMCP) and MCH did not elute separately from the column; therefore, c12DMCP formation rates were calculated from its equilibrium constant with t12DMCP at 473 K [18]. 13DMCP chemical isomers (c13DMCP and t13DMCP) were detected at a nearly constant ratio ([c13DMCP]/[t13DMCP] = 1.071 ± 0.008), leading us to assume similar equilibration for cis and trans 12DMCP. The c12DMCP and t12DMCP isomers (and the c13DMCP and t13DMCP isomers) are treated as a 12DMCP (and 13DMCP) lumped products. The concentration of any product (t12DMCP, c12DMCP, and ECP) present as trace impurities (<0.0013 mol%) in MCH reactants was subtracted from those detected in the effluent in determining product formation rates. The rates of formation of each product were also corrected for their approach to equilibrium for the reactions that form them from MCH using the following:

$$r_{forward} = r_{net}\left(1 - \left(\frac{P_P}{P_{mch}}\right)\frac{1}{K_{mch,P}}\right)^{-1} \tag{1}$$

in which (P_P/P_{mch}) is the ratio of product and MCH pressures in the effluent and $K_{mch,P}$ is their equilibrium constant at 473 K, derived from reported thermodynamic data [18,19]. Catalyst deactivation (half-lives between 14 and 72 ks) was observed on all catalysts dur-