Hydrodesulfurization on Transition Metal Catalysts: Elementary Steps of C-S Bond Activation and Consequences for Bifunctional Synergies

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Introduction
The practical importance of hydrodesulfurization (HDS) has led to its extensive study on transition metal catalysts and particularly on Co(Ni)Mo(W) sulfides. Elementary steps that mediate HDS and the role of bimetallic promoters remain controversial, in part because of the non-uniform structure of these layered materials and the concomitant challenges in their characterization. Here, we present kinetic analyses of thiophene HDS on S-saturated surfaces of monometallic isotropic clusters (Ru, Pt, Re) and lamellar sulfide nanostructures (FeS2), dispersed on SiO2, at practical HDS conditions. We find that the reactivity of these materials reflects elementary steps that involve the activation of the C-S bond, similar in nature to those required for metal-catalyzed cleavages of C-C and C-O bonds in alkane and alkanol hydrogeolyis. Such H-assisted activation of chemical bonds on these monofunctional sites (L1) determines whether rate enhancements are observed in bifunctional systems, wherein additional sites (L2) that are inactive for H2 dissociation and separated from L1 by insulating media (SiO2, γ-Al2O3), on which surface diffusion of neutral or charged H-atoms seems implausible, appear to contribute to increased rates of hydrogenation. These so-called “hydrogen spillover” effects are apparent on catalytic systems for which equilibrated formation of reactant-derived, molecular H-carriers occurs before the kinetically-relevant H-attachment step in the monofunctional route catalyzed by L1 sites; they arise from the gaseous diffusion of such molecular carriers and their transfer of hydrogen to reactants adsorbed on L2 (γ-Al2O3) sites.

Materials and Methods
Ru, Pt, and Re catalysts were prepared from inorganic precursors dissolved in aqueous solutions, deposited onto SiO2 by incipient wetness impregnation. After thermal treatment in flowing dry air, the resulting metal oxides were exposed to reducing (H2) or suliding (H2S/He mixture) environments to form well-dispersed metal clusters or sulfide layers, respectively. Characterization probes (transmission electron microscopy, X-ray absorption spectroscopy, reduction dynamics, X-ray diffraction, chemisorption) were used to determine the structure, phase, and dispersion of these catalysts before and after HDS reactions. Kinetic studies at relevant HDS temperatures (573-623 K) and pressures (1-3 MPa H2, 1-10 kPa thiophene, 0.2-15 kPa H2S) were performed in packed bed reactors with plug-flow hydrodynamics at differential conditions. Turnover rates in bifunctional systems for HDS (per g-atom of L1 sites) on intimate physical mixtures of SiO2-supported metal catalysts and high surface area (192 m2/g γ-Al2O3) were compared by defining a β′ parameter (m2 γ-Al2O3 (g-atom thiophene s-1)1/2), which reflects a measure of the maximum active L2 surface area normalized by the monofunctional rate, the latter as a surrogate for activity on L1 sites.

Results and Discussion
HDS on S-covered bulk metals (Ru, Pt, Re) and bulk metal sulfides (ReS2) of structure and stoichiometry confirmed by extensive characterization occurs via a similar sequence of elementary steps. Turnover rates increase sublinearly with H2 and thiophene pressures and decrease with increasing S-chemical potential (set by H2S/H2 ratios). All rate data are consistent with kinetically-relevant H-additions to bound thiophene (on Ru, Pt, ReS2) or monohydrothiophene (on Ru, Pt) species on surfaces covered with H2, thiophene, and S-species.

HDS selectivities to tetrahydrothiophene (THT) and C4 products are single-valued functions of conversion at all thiophene pressures and H2S/H2 ratios, even though the latter strongly influenced turnover rates, indicating that primary and secondary reactions occur on similar sites. The ratio of THT to C4 formation rates, extrapolated to zero conversion, increased with (H2)2/3, suggesting that intermediates leading to primary formation of THT contain one more H-atom than those involved in C-S cleavage. The rate of secondary THT conversion to C4 products was inversely proportional to H2 pressure, suggesting dehydrogenation was required. Such behaviors argue against THT as a reaction intermediate along the HDS pathway and indicate that it forms as an “over-hydrogenation” mistake, corrected by subsequent readsorption and dehydrogenation to the degree of unsaturation required to weaken the C-S bond, as also found for C-C and C-O cleavages on metals.

The presence of another function (γ-Al2O3) increased the rate of THT formation but only on those catalysts (Pt, Ru) for which the kinetically-relevant H-addition step for THT formation on L1 occurs after the additions of H-atoms required to form the H-carrier (I) that is responsible for transferring hydrogen to reactants adsorbed on L2 (Figure 1). These enhancements were more dramatic with increasing β′ until a point where bifunctional rates became limited by the formation of (I) on L1 (Pt and Ru, Figure 2), whereupon THT formation rates on L2 became sensitive to S-chemical potential similarly as monofunctional HDS rates were on L1, implicating the role of L1 in these bifunctional cascades. In contrast, on ReS2, enhancements that otherwise require the formation, desorption, and diffusion of (I) are not observed (Figure 2) because the first H-addition limits monofunctional HDS on these surfaces.

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References