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Prologue

From a trickle of papers in the early 80s, mostly concerning details of zeolite dehydrocyclodimerization processes such as Cyclar, the topic of post-transition metal-modified zeolites has blossomed. Because most of the research covered in the open literature in this area is still curiosity-driven rather than developmental in nature, perhaps we should reflect here on the reasons underlying the growth. The simplest reason might be that with so many groups already working on zeolites containing highly dispersed transition metals, or metal clusters, this field seemed a natural extension. But we would propose a further explanation as well: when new materials give tried and true concepts a new twist, everyone approaches the learning curve with less trepidation.

What we are referring to here is the idea that aromatization and associated reactions catalyzed by zeolites loaded with post-transition metals, in particular Ga or Zn, occur by a well-defined metal/acid bifunctional mechanism. However, in this case, the metal component does not have the usual properties associated with transition metal catalysis, and therefore the traditional metal/acid functionalities for hydrocarbon reactions are not necessarily applicable. In fact, the delineation of catalytic activity between the post-transition metal and acid functions is much less distinct. With all the work on these catalysts to date, the most important role of the post-transition metal for aromatization and other dehydrogenation/chain-building mechanisms is the formation and desorption of H_2, and this property is perhaps the only important property universally agreed upon. Iglesia and co-workers formalized this concept, tying the equilibrium limitations of dehydrogenation on zeolites to the 'surface fugacity' or 'virtual pressure' concepts of Temkin, Boudart and others [1]. Even the *n*-alkane to alkene dehydrogenation is still a subject of controversy regarding whether acid or metal functions are required for this step, and of some of the subsequent papers consider this point. Another important twist on the old concepts was the discovery that gallium cations can replace protons in the zeolite, which has major ramifications on the metal/acid balance [2].

So although the mechanistic proposals in this field hearken back to old debates over the differing functions of acid sites and metal crystallites in reforming catalysis, the old classifications don't exactly apply. For example, if we try to apply Weisz's concept of a 'trivial' vs. 'nontrivial' polystep reaction [3], that is, nontrivial denoting a pathway:

$$A \Rightarrow B \Rightarrow C$$

which is equilibrium-limited in B with the second reaction catalyzed by a different function than is the first, it is apparent that, say, propane to aromatics catalyzed by a Ga-loaded zeolite would be considered 'trivial' by Weisz's original classification because the thermodynamic equilibrium constants, computed on a gas-phase basis, of all of the constituent reactions are adequate for high overall conversion. In this case, however, propane conversion is in fact nontrivial, because of the inadequacy of acidic zeolites in the H-atom recombinations which must occur in the absence of hydrocracking. One surprising feature, though, is the apparent

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distance which can exist between the two catalytic functions, seemingly in violation of Weisz's intimacy criterion developed for reforming catalysts [3], because mechanical mixtures of post-transition metal oxides with the acidic form of the zeolite can yield very effective catalysts for aromatization reactions. Are the diffusivities of the H-atoms in zeolites really so high, the H-atom recombination activities of a few contact metal sites really so great, or the distances shorter and metal dispersions higher than the state initially prepared? All these questions are considered by the authors of these papers, and in addition other potential uses for these materials are proposed.

As a final caution we might do well in the future to critically examine some of the more specific bifunctional mechanisms proposed for the action of these catalysts in dehydrogenation/aromatization and other chain-building reactions. In this regard we should remember some of the early history of the study of Pt reforming catalysts. It was at one time thought that essentially all isomerization, cyclization and hydrocracking reactions took place on acid sites only [4]. While still a useful concept today, especially with industrial feeds where the metals are typically sulfided and coked to the extent that only the simplest of dehydrogenation reactions may occur on the Pt sites of a commercial reforming catalyst [5,6], no one would now deny that essentially all conventional reforming reactions can take place on appropriate Pt sites, such reactions including cyclization [6,7,8,9], isomerization of either small [10] or mid-range alkanes (by either cyclic or bond-shift mechanisms) [11,12], or C–C bond rupture [13,14]. It is especially relevant that some of these reactions were barely measurable (for Pt) unless the correct dispersion or surface structure were present [10,15,16,17]. Such could also be the case with the subject catalysts of this volume, especially as more information on highly dispersed (metal cation) preparations emerges.

In arranging this special edition, we have placed the two papers dealing with emerging areas of post-transition metal catalysis first. Subsequent papers all deal with hydrocarbon conversion, and we have tried to place them in topical proximity to one another, though such a task was impossible to perform perfectly because of the diversity of the topics covered. We would like to thank all the authors who contributed to this special edition, and congratulate them on an important open discussion.

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