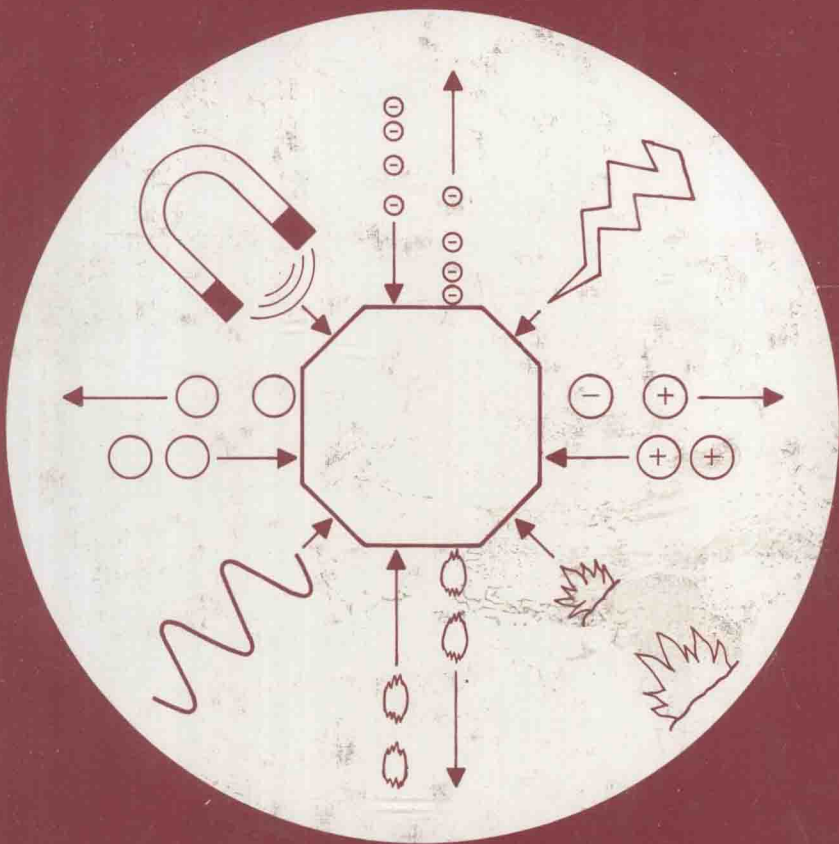


studies in surface science and catalysis



46

ZEOLITES AS CATALYSTS, SORBENTS AND DETERGENT BUILDERS

Applications and Innovations

**H.G. Karge
J. Weitkamp**
(editors)

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**Proceedings of an International Symposium, Würzburg, F.R.G.,
September 4–8, 1988**

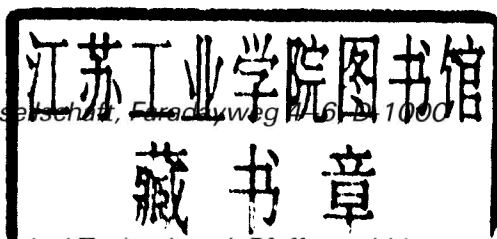
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PREFACE

This symposium was one of the smaller zeolite meetings held in between the big International Zeolite Conferences. It is the latest in the series of meetings which started in 1978 in Szeged, Hungary, and continued in 1980 in Villeurbanne (Lyon), France; 1982 in Bremen, FRG; 1984 in Prague, Czechoslovakia; 1985 in Siófok, Hungary; and 1987 in Nieuwpoort, Belgium. These conferences are intended to cover selected fields from the broad area of zeolite research and application. For the Würzburg Symposium emphasis was placed on zeolite catalysis, sorption and detergent builders. With respect to catalysis, particular attention was paid to the synthesis of fine chemicals with the help of zeolite catalysts. An overview of this important field was given in two invited lectures which were complemented by a number of related oral and poster contributions. Special efforts were made to bring together experts from industry and academia. This endeavour was successful, as was reflected both in the invited lectures, oral and poster presentations and in the composition of the audience. An expected trend was the ever increasing interest in the so-called new generation molecular sieves both for research and application. A remarkable number of the presented studies were devoted to these materials. Innovations, however, were mostly visible in developing and refining methods and techniques of investigation either in experiment or theory. Obviously, successful application of highly sophisticated tools of solid state and surface science to problems of zeolite research now becomes possible. This seems to promise a growth in our knowledge of and deeper insight into the subtle details of zeolite properties and behaviour.

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January, 1989

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The organizers of the international Symposium on "ZEOLITES AS CATALYSTS, SORBENTS AND DETERGENT BUILDERS", held at Würzburg, Federal Republic of Germany, September 4-8, 1988 express their appreciation to the members of the International Scientific Committee who carried out the difficult and important task of paper selection.

They also wish to thank the members of the Executive Staff for their great efforts made during preparation and running of the symposium. Particular thanks are due to Mrs. R. Stottko for the coordination and execution of the finances, to Dr. St. Ernst for his active participation in the organizational work and to Mrs. M. Rahimi, Mrs. E. Stankewitz and Mrs. J. Reiffel for their most valuable assistance in preparing the proceedings.

Furthermore, the organizers thank the authors for submitting their manuscripts for publication in these proceedings and the referees for spending time and effort in order to ensure the high scientific standard of the contributions.

Last but not least, the help and generous financial support of collaborating organizations and sponsors from the industry is gratefully acknowledged.

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SKELETAL REARRANGEMENT REACTIONS OF OLEFINS, PARAFFINS AND AROMATICS OVER ALUMINOPHOSPHATE BASED MOLECULAR SIEVE CATALYSTS

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ABSTRACT

Medium pore aluminophosphate based molecular sieves with the -11, -31 and -41 crystal structures are active and selective catalysts for 1-hexene isomerization, hexane dehydrocyclization and C₈ aromatic reactions. With olefin feeds, they promote isomerization with little loss to competing hydride transfer and cracking reactions. With C₈ aromatics, they effectively catalyze xylene isomerization and ethylbenzene disproportionation at very low xylene loss. As acid components in bifunctional catalysts, they are selective for paraffin and cycloparaffin isomerization with low cracking activity. In these reactions the medium pore aluminophosphate based sieves are generally less active but significantly more selective than the medium pore zeolites. Similarity with medium pore zeolites is displayed by an outstanding resistance to coke induced deactivation and by a variety of shape selective actions in catalysis. The excellent selectivities observed with medium pore aluminophosphate based sieves is attributed to a unique combination of mild acidity and shape selectivity. Selectivity is also enhanced by the presence of transition metal framework constituents such as cobalt and manganese which may exert a chemical influence on reaction intermediates.

INTRODUCTION

According to recent reports, the aluminophosphate based molecular sieves have acidic catalytic activity for a broad array of petroleum refining and petrochemical reactions. In early studies (ref. 2) n-butane cracking activities were reported for a number of silicoaluminophosphate (SAPO) molecular sieves. These SAPO molecular sieves showed weak acidity by comparison with zeolites. Subsequently, it was found that transition metal substitution into certain aluminophosphate crystals resulted in enhanced acidity as indicated by enhanced butane cracking activity (ref. 3). With medium pore species the generally mild acidity combined with unique shape selectivity has resulted in improved catalytic selectivity in several reactions. Thus, a review of the patent literature reveals that aluminophosphate based molecular sieves have shown catalytic activity in fluid catalytic cracking (ref. 4), hydrocracking (ref. 5), dewaxing (ref. 6), reforming (ref. 7), aromatic alkylations (ref. 8), methanol to olefin conversion (refs. 9,10) and in olefin oligomerization (refs. 8,11). In several cases olefins play an important role, either as feed constituents or

as reaction intermediates. The enhanced selectivity of certain SAPO's for olefin reactions has already been noted. Thus, small pore SAPO's, such as SAPO-34, were found very effective at interconverting light olefins such as ethylene, propylene and butylenes with little loss to paraffinic or oligomeric products (ref. 12). The medium pore SAPO's were also active and very selective for oligomerization of propylene and butenes to olefinic gasoline (ref. 11) or to distillates without the production of paraffins or aromatics.

The present paper reports on the catalytic properties of selected aluminophosphate molecular sieves in model hydrocarbon reactions. The molecular sieves were selected to represent large and medium pore sizes with a variety of framework elements including transition metals, in addition to aluminum and phosphorus. Model reactions were chosen to explore catalytic performance in paraffin, olefin and aromatic rearrangement reactions to probe molecular sieve character, shape selectivity and catalytic activity, particularly for reactions involving olefins or olefin reaction intermediates.

EXPERIMENTAL

Molecular Sieve Catalyst Preparation

The aluminophosphate based molecular sieves used in the present study were prepared according to procedures described in US Patent (refs. 2, 13, 14). The preparation of medium pore reference molecular sieves, LZ-105 zeolite and silicalite, have also been described elsewhere (refs. 15, 16).

For 1-hexene isomerization and for acid catalyzed C_8 aromatic reactions all molecular sieves were evaluated in their calcined, powdered state. For the study of C_8 aromatics, selected SAPO molecular sieves were aluminum exchanged or steam treated as noted in Table IV. For bifunctional catalysts used in paraffin cyclization/isomerization and ethylbenzene-xylene interconversions, the calcined molecular sieve powder was mixed with platinum-loaded chlorided gamma alumina powder. These mixtures were then bound using silica sol and extruded to form 1/16" extrudates which were dried and calcined at 500°C. The bifunctional catalysts were prepared to contain about 0.5% platinum and about 40 to 50% SAPO molecular sieve in the finished catalysts.

Catalyst Evaluation

The powdered molecular sieves were evaluated following the treatment described above, without further activation. The 1-hexene isomerization and C_8 aromatic isomerization tests were conducted in tubular, fixed bed, continuous flow microreactors. The catalyst bed contained one gram molecular