科技资料

Synthesis & Properties of New Catalysts: Utilization of Novel Materials Components & Synthetic Techniques

EXTENDED ABSTRACTS
(EA-24)

Synthesis and Properties of New Catalysts: Utilization of Novel Materials Components and Synthetic Techniques

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Proceedings of Symposium S
1990 Fall Meeting of the Materials Research Society
November 26 - December 1, 1990
Boston, Massachusetts

Symposium Support:

Air Products and Chemicals, Inc.
American Chemical Society Petroleum Research Fund
Amoco Oil and Chemical Companies
Exxon Chemicals, Inc.
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Mobil Research and Development Corporation
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Pechiney Corporation
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Extended Abstracts

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Published by:

Materials Research Society
9800 McKnight Road
Pittsburgh, PA 15237
telephone: (412) 367-3003
fax: (412) 367-4373

Manufactured in the United States of America

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Preface

The range of catalytic materials is constantly expanding, largely through the identification of new synthetic components and synthetic methods. One of the results of this growth has been the evolution of improved catalyst characterization and evaluation techniques which have matured at a comparable rate. The focus of this symposium was to discuss recent developments in each of these areas as they related to the synthesis and identification of new classes and types of catalytic materials. These reports have been organized into seven sections for this compendium: microporous materials, layered materials, oxides, carbides, sulfides, nitrides, and metals in catalysis.

The editors would like to thank the contributing authors whose efforts were responsible for the success of this symposium. They would also like to graciously acknowledge the generous support the symposium received which enabled a truly international exchange of information by leaders in various fields of catalysis. The responsible organizations include:

Air Products and Chemicals, Inc.
American Chemical Society Petroleum Research Fund
Amoco Oil and Chemical Companies
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Exxon Research and Engineering Company
W.R. Grace and Company, Research and
Davison Chemical Divisions
Mobil Research and Development Corporation
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Finally, we would like to thank our own organizations for allowing us to devote our time to this symposium.

Edward W. Corcoran, Jr.
Marc J. Ledoux

November 1990

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Part I

Microporous Materials

PROGRESSES IN SYNTHESIS AND CHARACTERIZATION OF LARGE AND VERY LARGE PORE (SILICO)ALUMINOPHOSPHATE MOLECULAR SIEVES : SAPO-37, SAPO-40, AND VPI-5/MCM-9

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INTRODUCTION

Because of their potential interesting and attractive applications in catalysis and adsorption, the synthesis and characterization of (silico)aluminophosphates with large (e.g. SAPO-37) or extra large (e.g. VPI-5 or MCM-9) pore structures recently aroused increasing attention. SAPO-37 involves a Faujasite-type topology [1], while VPI-5 [2] and its SAPO structural analogue, MCM-9 [3], constitute a new group of molecular sieves with channels limited by 18T membered rings.

In this review, we briefly present the highlights of our recent general study of the synthesis routes leading to pure, highly crystalline SAPO-37 [4-7], VPI-5, and MCM-9 [8]. Slight modifications of their crystallization conditions favor the co-crystallization of other phases, such as SAPO-40 [4-7] or SAPO-11 [8]. We also discuss some specific conditions under which SAPO-37 undergoes structural degradation [6, 7, 9] and under which VPI-5 transforms into another structurally related porous phase, namely $AlPO_4$-8 [10-11].

SYNTHESIS AND CHARACTERIZATION OF SAPO-37 AND SAPO-40

SAPO-37 can crystallize in two different synthesis media: a single aqueous liquid phase reaction mixture and a two-liquid phase synthesis system [4,5].

The conventional "aqueous route" consists in heating, at 200°C, a hydrogel, prepared by mixing, in an appropriate way, orthophosphoric acid, water, aluminum oxide, fumed silica and tetrapropylammonium- and tetramethylammonium hydroxides, as structuring agents, and aged for 48h.

Aging and heating times, as well as the stirring conditions have a determinant effect on the crystallization course. Aging under stirring favors the rapid nucleation and growth of pure SAPO-37, while the absence of aging and stirring, as well as long synthesis times promote the co-crystallization of a side-phase, SAPO-40.

In the new "biphasic route", SAPO-37 is prepared from a two-liquid phase reaction mixture containing the required reactants dissolved either in a liquid organic (typically hexanol) or in an aqueous phase. A thorough stirring of the mixture is needed for the ingredients of both phases to mix and react. One of the advantages of this approach consists in a progressive generation of the silica species by the slow hydrolysis of tetraethylorthosilicate dissolved in hexanol and in their homogeneous

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incorporation in the growing crystallites.

In order to evidence the successive steps occurring during the crystallization process of SAPO-37 in aqueous medium, a series of intermediate phases were isolated and characterized by XRD, SEM and multinuclear NMR [6,7]. NMR of adsorbed xenon was particularly efficient to detect, at the early stages of the crystallization, the presence, in the gel, of preliminary void structures that could not be evidenced by XRD or SEM. Upon heating at 200°C, well defined octahedrally shaped SAPO-37 crystals nucleate at the interface of the highly restructurated gel. ^{27}Al- and ^{31}P- NMR spectra of the successive intermediate phases illustrate the progressive incorporation of Al and P in configurations Al(4P) and P(4Al) of the SAPO-37 framework, , at the expense of the amorphous phase. The chemical shifts of some of the ^{27}Al- and ^{31}P-NMR lines and their sensitivity to calcination suggest that the coordination state of some (otherwise tetrahedral) framework Al and P atoms is modified, due to non negligible interactions of these atoms with the neighbouring occluded organic molecules. As we evidenced by ^{129}Xe-NMR [9] and XRD [7], SAPO-37 devoid of this original organic molecules content (i.e. SAPO-37 in its H-form) is very unstable in wet atmosphere: the formation of large cavities and a partial pore blockage, due to the partial structure collapse, lead to a dramatic decrease of the sorption capacity. The crystallinity reaches a maximum after 32h of heating at 200°C. For longer crystallization times, the SAPO-37 network undergoes a partial degradation, as evidenced by XRD and ^{129}Xe-NMR, accompanied by the formation of $P(OH)_n$ and $Al(OH)_n$ terminal defect groups, as detected by ^{31}P- and ^{27}Al-NMR, respectively. Such defects easily recombine by successive calcinations at 550°C. In contrast to SAPO-37 that stems from a direct gel restructuration, the side-phase SAPO-40 (platelet-like crystallites) co-crystallizes from the mother liquid phase, probably because of the marked change in its nature and composition occurring during the prolonged heating at 200°C.

Distinct ^{129}Xe-NMR signals characterize these two SAPO materials. We took advantage of this technique to determine, more accurately than by XRD, the wt. % of SAPO-40 admixed with SAPO-37. Moreover, by comparing the chemical shift values of the ^{129}Xe-NMR resonance of SAPO-40 with those recorded for various other molecular sieves (e.g. SAPO-37 and ZSM-5), the corresponding pore volumes, estimated by n-hexane adsorption, and the restrictions to diffusion, we were able to propose a structure for SAPO-40. It possibly involves a tridimensional network consisting of interconnected straight channels limited by 12T puckered rings.

The combined use of high resolution solid state MAS ^{29}Si-, ^{27}Al- and ^{31}P-NMR allowed us to investigate the short range structural configuration and coordination of Si, Al and P, and their distribution in the SAPO-37 framework, as well as the mechanisms governing their potential substitution in a hypothetical Faujasite $AlPO_4$ structure [5]. When larger amounts of silicon are introduced in the gel, more siliceous SAPO-37 materials are formed, in the framework of which the distribution of Si is heterogeneous [5]. We have evidenced three distinct regions, each being characterized by specific Si(nAl) configurations: a SAPO-domain, a silica-rich zeolite region (silica islands) and a zeolitic Faujasite-type region with Si/Al = 1.6. The Si content of each domain can be estimated from the relative intensities of the ^{29}Si-NMR lines belonging to each configuration.

SYNTHESIS AND CHARACTERIZATION OF MCM-9, the Si-ANALOGUE OF VPI-5

MCM-9, the silicon-containing analogue of the extra large pore molecular sieve VPI-5, was synthesized using a two-liquid (aqueous and immiscible organic) phase synthesis medium [8]. The Si incorporation into the aluminophosphate framework is achieved by the phase transfer and hydrolysis of a Si-containing reagent (typically tetraethylorthosilicate), supplied from the immiscible organic phase. Aging of the aluminophosphate precursor gel before and after the addition of di-n-propylamine (structure directing agent), rather low autogeneous crystallization temperature (140°C) and a short crystallization time (2h) are among the conditions required to yield MCM-9 with a minimum of impurities. Traces of SAPO-11 or of H3 phase appear as side-compounds, as soon as these optimized conditions are slightly changed. Thermal analysis data indicate that the structure of MCM-9 is stable to at least 500°C in dry air. Treated in this way, this material shows molecular sieve properties corresponding to 18T circumscribed channels having 12Å pore openings, as evidenced by ^{129}Xe-NMR measurements [12].

TRANSFORMATION OF MCM-9/VPI-5 INTO SAPO-8/AlPO$_4$-8 UNDER VARIOUS POST SYNTHESIS TREATMENTS [10-11]

VPI-5 or MCM-9 materials can partially or integrally transform into AlPO$_4$-8 or SAPO-8, under specific post-synthesis treatments, such as washing and drying steps [11]. The transformation may be reversible and strongly depends on the evacuation and rehydration treatments, on the heating rate, and probably on the lattice defect concentration [10]. The critical parameter favoring the transition appears to be the progressive loss of water at a temperature equal to or higher than 100°C. The removal of water at low temperatures (e.g. -30°C or +20°C) maintains the original VPI-5/MCM-9 structure, even if the product is pre-boiled at 100°C for several hours. Transition intermediates were detected by ^{31}P-NMR. From the knowledge of the VPI-5 and AlPO$_4$-8 structures [13-14], we have reassigned all the ^{31}P-NMR lines characterizing both materials and explained further the effect of water on the dramatic changes occurring in the ^{31}P- and ^{27}Al-NMR spectra of the transition intermediate structures, compared with those of AlPO$_4$-8 and VPI-5. ^{31}P- and ^{27}Al-NMR have been used to determine which specific T sites undergo modification, and we were able to propose a complete mechanism accounting for the transformation [10].

We further proposed a model allowing us to determine the degree of