Preface

The interest in all aspects related to pillared interlayered clays, such as new synthesis methods or the study of their properties and applications, has greatly increased over the last few years. Several of the papers devoted to pillared interlayered clays, both as articles and as book chapters, have reviewed various aspects of the preparation, characterization, or applications of these solids. The approach that has been commonly used in previous studies to organize such a large amount of information is mainly based on the preparation of pillared clays, as well as some aspects about the catalytic applications of these solids. As indicated earlier, the interest in these solids is so large that, since our first comprehensive review on the synthesis and catalytic applications published 9 years ago (Gil A, Gandia LM, Vicente MA (2000) Recent advances in the synthesis and catalytic applications of pillared clays. *Catalysis Reviews*, 42:145–212), more than 500 new references have appeared in the literature and interest in this field is continuously increasing. A second review deals with the porous structure developed by these materials during the intercalation process (Gil A, Korili SA, Vicente MA (2008) Recent advances in the control and characterization of the porous structure of pillared clay catalysts. *Catalysis Reviews*, 50:153–221). This is a very important aspect because the textural properties of pillared clays play a key role when these materials are used as catalysts, adsorbents, or in gas separation.

Since the first works introducing the aluminum intercalated clay family at the beginning of the 1970s, the synthesis of pillared interlayered clays has expanded enormously. The need for solids that could be used as cracking catalysts with larger pores than the zeolitic materials spurred the synthesis of new porous materials from clays. These solids are prepared by exchanging the charge-compensating cations present in the interlamellar space of the swelling clays by hydroxyl-metal polycations. On calcining, the inserted polycations yield rigid, thermally stable oxide species, which prop the clay layers apart and prevent their collapse. The intercalation and pillaring processes produce the development of a porous structure with the presence of particular surface sites. These properties determine the potential use of the solids in catalytic, purification, and sorption-based separation applications. The properties of pillared clays synthesized in the presence of microwave irradiation are compared to those prepared in the conventional way by Fetter and Bosch in

Chapter 1. In Chapter 2, Pires and Pinto present the potential use of pillared clays as selective adsorbents of natural and biogas components, such as carbon dioxide, methane, ethane, and nitrogen.

An important characteristic of the pillared clays is their acidity. The type, number, and strength of surface acid sites depend on several factors, such as the exchange of cations, the preparation method, and the nature of the starting clay. These are properties directly related to the catalytic performance. Therefore, the type of acidity can determine which type of reaction the clays can catalyze. Several types of reaction have been studied, such as alkylation, dehydrogenation, hydrocracking, and isomerization. Some examples of this type of applications are summarized in Chapters 3 and 4.

One of the most studied topics related to pillared clays is their use as supports for catalytically active phases, and the use of the resulting solids in several reactions, particularly in environment-friendly ones. The number of articles in this field is very extensive, including catalysts that contain Co, Cr, Cu, Fe, Mn, Ni, Pd, Pt, Rh, or V. Mishra summarizes the synthesis and applications of transition metal oxide-pillared clays in Chapter 5. Titanium, iron, chromium, manganese, and mixed oxides were considered, with emphasis on their future potential as catalysts. Hydrocarbon cracking and various examples related to environmental processes as photocatalysis and pollution control in gas and liquid phases are presented by the author. The use of pillared clays in catalytic waste water treatment is summarized in Chapters 6–8. Herney-Ramirez and Madeira reviewed the use of pillared clays in heterogeneous Fenton-like advanced oxidation processes. The effect of the main operating conditions on oxidation efficiency is considered by the authors. Special attention to the use of pillared clays in wet air catalytic oxidation (WACO), wet hydrogen peroxide catalytic oxidation (WHPCO), and photo-Fenton conversion of pollutants is considered by Perathoner and Centi. The catalytic wet peroxide oxidation of phenol using pillared clays in a continuous flow reactor is presented by Guélou et al. in Chapter 8. The experimental results are very promising for developing a catalytic continuous process for industrial wastewater purification. The chapter written by Zuo et al. reviews the recent developments offered from pillared clay-supported noble metals and metal oxide catalysts for complete oxidation of representative volatile organic compound (VOC) molecules such as benzene, toluene, chlorobenzene, phenol, among others. Selective reduction of NOx has been the reaction *to* environmental interest for which pillared clays have been most widely used. Recent trends, limits, and opportunities offered from pillared clays and other related materials (layered clays, layered double hydroxides (LDHs), and porous clay heterostructures (PCHs) in this field are discussed by Belver in Chapter 10. Special attention is focused on the modification that led to materials with a higher or comparable activity to that described by commercial systems. In Chapter 11, Vicente et al. presents the use of pillared clays in catalytic oxidation reactions related to green chemistry concepts.

The book also includes four Chapters (12–15) dealing with treatment of other layered materials, mainly anionic clays, and mesoporous solids, comparing them with the pillared clays. The state-of-the- art in the synthesis, characterization, and catalytic performance of layered double hydroxides (LDH) with the hydrotalcite-type structure containing several polyoxometalates (POM) in the interlayer is presented by the Rives group in Chapter 12. The immobilization of polyoxometalate species in the interlayers of layered double hydroxides with the hydrotalcite-type-solids allows the preparation of homogeneous catalysts with tailored redox and acidity properties. The authors indicate that the properties of these materials can be finely tuned through the modification of the cations in the brucite-like layers and the polyoxometalate in the interlayer, in order to apply them to several catalytic processes. Other parameters such as the polarity modulation or the solvents can modify the reactivity of the LDH–POM catalysts. In Chapter 13, Figueras presents the latest ideas on the modification of the basic properties of hydrotalcites by anion exchange and on the properties of solid bases as catalysts. Several examples of applications are given, with emphasis on industrial processes recently shown such as isomerization of olefins, aldolization, oxidation of ketones; supports of metal catalysts; as well as adsorbents and anionic exchangers. The synthetic pathways for obtaining mesoporous phosphate structures and aluminophosphates make up the subjects presented in Chapters 14 and 15 by Moreno et al. and O'Malley et al., respectively. The preparation of metal-supported catalysts and their application in gas separation, adsorption, and catalysis are also reviewed.

In the final chapter, the synthesis and application to industrial catalytic reactions of macrocyclic complexes supported on clays with thermal and chemical stability are presented by the team of Kumar et al.

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