

Genesis of Acid–Base Support Properties with Variations of Preparation Conditions: Cumene Cracking and Its Kinetics

Fernando Trejo,^{*,†} Mohan S. Rana,[‡] and Jorge Ancheyta[§]

[†]Centro de Investigación en Ciencia Aplicada y Tecnología Avanzada Unidad Legaria del Instituto Politécnico Nacional (CICATA-IPN), Legaria 694, Col. Irrigación, México DF 11500, México

[‡]Petroleum Refining Department (PRD), Kuwait Institute for Scientific Research, P.O. Box 24885, Safat 13109, Kuwait

[§]Instituto Mexicano del Petróleo, Eje Central Lázaro Cárdenas Norte 152, Col. San Bartolo Atepehuacan, México DF 07730, México

ABSTRACT: Mixed oxides (Al–Si, Zr–Si, Mg–Si) were synthesized by the sol–gel method at different gelation times. The synthesized supports were impregnated by the incipient wetness method to obtain Ni–Mo, Co–Mo, and Ni–W supported catalysts. Both the supports and catalysts were characterized by N₂ physisorption for determining textural properties, and their catalytic activities were tested with isopropyl alcohol (2-propanol) and cumene decomposition in order to evaluate their acid–base properties. According to the obtained products, it was possible to assess qualitatively that Al–Si and Zr–Si supports and their respective catalysts were mainly acidic. In the case of NiMo/AlSi catalyst, high conversion during cumene cracking particularly at higher temperatures was observed. Cracking activity results indicated that surface acidity predominated due to Brønsted acid sites, which are mainly dependent on the support composition as well as their preparation methods. Conversion of isopropyl alcohol leads to the dehydration products, typically propylene with a very low amount of di-isopropyl ether or acetone. NiMo/AlSi catalyst was evaluated for cumene cracking and its kinetic parameters were obtained by applying the Langmuir–Hinshelwood model. The activation energy was found to be 27.75 kcal mol^{−1} while the heat of adsorption calculated with the Van't Hoff equation was −14.15 kcal mol^{−1} taking into account a single-site surface reaction.

1. INTRODUCTION

The demand for stringent environmental regulations of clean fuels is focusing the attention of researchers as well as refiners to the hydrotreatment of various petroleum fractions using new catalytic materials and the development of new and more efficient processes.^{1–3} The use of mixed oxides (SiO₂–Al₂O₃, SiO₂–ZrO₂, SiO₂–TiO₂) as supports has become very attractive with respect to their textural properties and interaction with active metals.^{4,5} Oxides used as catalysts have the ability to take part in the exchange of electrons or protons in both redox and acid–base catalysis.⁶ In metal oxides, coordinative unsaturation is principally responsible for the adsorption and catalysis of various reactions. The exposed cations and anions of the metal oxide surfaces form acid and basic sites as well as acid–base pairs. The catalytic activity of acidic solids is not only related to the surface concentration of acid sites, but also depends on their nature, that is, being Brønsted or Lewis sites.⁷

Amorphous silica-based mixed metal oxides such as silica–alumina and silica–zirconia are widely used as acidic catalysts, and their properties depend on the preparation procedure. Silica-based amorphous mixed oxides supports have been studied, and their preparation methods are reported in the literature.^{8–10} Usually, oxide properties depend on the preparation procedure which affects textural properties mainly. The sol–gel method is one of the most important applications available in heterogeneous catalysis. Generally, supports obtained by using the sol–gel method have high porosity, large specific surface area, and acid sites that make them very attractive.⁶ This method has attracted great interest in the past few years since it is convenient to prepare supports where heteropoly condensation of different metals is responsible for the formation of metal–O–Si (M–O–Si)

strong bonds, which control the support particle size and distribution of metal particles in the solid matrix.¹¹ This method involves hydrolysis of an alkoxide followed by a condensation reaction to form a gel,¹² which is obtained by aging, drying, and calcination. It has been reported that bimodal catalysts (meso and macroporous) can be obtained with the use of tetraethyl orthosilicate (TEOS) and polyethylene oxide (PEO) by spinodal decomposition.¹³

A common way to evaluate acidic properties of supports/catalysts is during cumene cracking which has been reported in the literature to be a reaction for the simultaneous determination of Brønsted as well as Lewis acidity; however, it has been also stated that acidity of catalysts is modified during sulfidation which may also influence the catalyst activity. The cracking of alkylbenzenes is catalyzed by Brønsted acid sites, particularly during conversion of cumene into benzene and propylene which is a well-known reaction.¹⁴ Cumene cracking is enhanced by the acidity of mixed-oxide supports where the Mo-supported catalysts are more active than the support only. This is due to the presence of –SH groups on the catalysts and the exchange protons from the molybdenum sulfide phase as reported by Topsøe.¹⁵ Sarback¹⁶ studied the cumene decomposition over alumina modified with fluoride ions obtaining benzene and propylene as products, whereas alumina modified with sodium ions yielded α -methyl

Special Issue: IMCCRE 2010

Received: April 2, 2010

Accepted: June 15, 2010

Revised: June 14, 2010

Published: July 8, 2010