Synthesis and characterization of mesoporous Co-Pb/SBA-15 catalysts

M. Can[a], O. Guner[a], B. Akca[a], A. Yılmaz[b], M. Akcay[c] and D. Uner[a*]

[a]Chemical Engineering Department, Middle East Technical University
[b]Chemistry Department, Middle East Technical University
Ankara, 06531 Turkey
[c]Chemistry Department, Dicle University, Diyarbakir, 21280 Turkey
[*]uner@metu.edu.tr

Introduction

Mesoporous materials are porous materials with pore diameters in the range of 2-50 nanometers [1]. These materials have important applications in a wide variety of fields such as separation, catalysis, adsorption and advanced nanomaterials [2]. SBA-15 is by far the largest pore size mesoporous material with highly ordered hexagonally arranged mesochannels, with thick walls, adjustable pore size from 3 to 30 nm, and high hydrothermal and thermal stability [2]. By adding noble metals or metal oxides, physical and chemical properties of mesoporous materials are improved [3]. This study presents preparation and characterization of pure SBA-15, Co and/or Pb/SBA-15 mesoporous catalysts to be used for hydrogen production from methane by direct partial oxidation. Co-Pb mixed oxide catalysts have been shown to have superior oxidation abilities. The catalyst is prepared in a mesoporous framework of SBA-15 to improve the surface area and to stabilize Pb [4].

Materials and Methods

SBA-15 type catalysts were prepared according to the literature [5]. In order to prepare pure SBA-15 molecular sieve, 9 ml of tetraethyl orthosilicate (TEOS) was added to 150 ml of 1.6 M HCl solution containing 4 g triblock poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (EO_{20}-$PO_{70}EO_{20}$, Aldrich). The mixture was stirred for 24 h at 40 ˚C and was allowed to react at 100 ˚C overnight in Teflon bottles. The solid material obtained after filtering was finally calcined in air flow at 500 ˚C for 5h. In the preparation of the cobalt modified SBA-15, an appropriate amount of cobalt was introduced simultaneously with TEOS in the form of cobalt chloride ($CoCl_2 \cdot 6H_2O$, Merck). Pb modified catalyst was prepared similarly introducing lead in the form of lead acetate ($(CH_3COO)_2Pb \cdot 3H_2O$, Riedel-de Haen) simultaneously with TEOS. Different loadings of catalysts were prepared with respect to content of SiO_2. The characterization of the synthesized samples was done by *in-situ* FTIR, XRD, N_2 adsorption isotherms, TEM images and XPS analysis.

Results and Discussion

Acidity characterization and adsorption characteristics of Co and Pb doped SBA-15 samples at different weight loadings were investigated by in situ Fourier Transform Infrared Spectroscopy, FTIR, following adsorption of pyridine. Three modes of adsorption have been observed; electron transfer at Lewis acidic surface sites, proton transfer at Bronsted acidic surface sites and hydrogen bonding to surface hydroxyl groups. All of the samples showed both Lewis acidity and Bronsted acidity, but Bronsted acidity of the samples was stronger than their Lewis acidity.

X-ray diffractograms of both pure and Pb loaded SBA-15 samples did not exhibit any characteristic peaks for 5, 10, 15 wt %Pb loadings in the wide angle region (2θ= 5-75°) This indicated that Pb is finely dispersed on the surface of the sample or incorpareted in the pore walls of SBA-15. On the other hand, addition of Co resulted in formation of crystallites even at 5% loading [6].

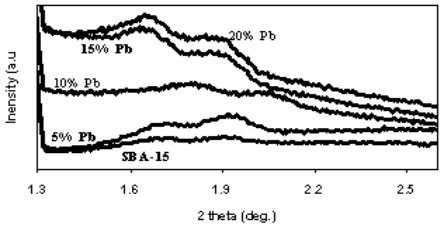

Figure 1. Small angle XRD patterns of Pb loaded SBA-15

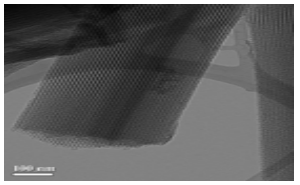

Figure 2. TEM images of pure SBA-15

Figure 1 shows small angle XRD patterns of Pb loaded SBA-15. The ordered hexagonal structure of SBA-15 is confirmed by typical diffractions for both Pb abd Co lodings. The increase in the loadings of metals in SBA-15 causes a decrease in the surface area due to the substitution of pores with metal atoms [6]. A TEM image of SBA-15 is shown in Figure 2. The TEM image confirms the ordered structure of the material, and shows the cylindrical pores are arranged in an ordered hexagonal array. XPS in the single doped cases indicated that binding energies of O 1s and Si 2p did not change much, while mixed oxide loaded samples showed higher binding energies indicating more intimate interaction of these metals with silica framework. Work is in progress to determine oxygen and methane adsorption desorption characteristics of these materials. The results of adsorption measurements will be consolidated with the XPS analysis and acid site characterization studies for identifying the optimum loading.

Acknowledgements:
Assistance in TEM measurements by Galen Stucky group of UC Santa Barbara is kindly appreciated.TUBITAK supported this project under grant 104T181. METU supported this work via OYP (BAP-08-11-DPT.2002 K 120510) and METU BAP 2006-03-04-05 projects.

References:

[1] Xia, Y. and Mokaya, R., J. Mater. Chem. **13**, 3112–3121 (2003)
[2] L. Qingyi, G. Feng, K. Sridhar, E. M. Thomas, J. Am. Chem. Soc. 126 (2004) 8650.
[3] J. Arbiol, A.Cabot, J. R. Morante, F. Chen, M. Liu, Appl. Phys. Lett. 81 (2002) 3449.
[4] D. Uner, M.K. Demirkol, B. Dernaika, Appl. Catal. B-Environ. 61 (2005) 359.
[5] D. Zhao, Q. Huo, J. Feng, B. F. Chamelka, G. D. Stucky, J. Am. Chem. Soc. 120 (1998) 6024.
[6] B.Akça, M. Can, V.Değirmenci, A.Yılmaz, D.Uner, *Studies in Surface and Science and Catalysis*, In press.