DEACTIVATION OF SOLID ACID CATALYSTS FOR ETHANOL DEHYDRATION REACTION

Orsina Verdes, Alexandru Popa, Mariana Suba, Silvana Borcanescu, Viorel Sasca

"Coriolan Drăgulescu" Institute of Chemistry Timisoara, BV. Mihai Viteazul nr. *24* 300223 *Timişoara, Romania*
e-mail: orsinaverdes@yahoo.com

Abstract

Heteropolycompounds (HPCs) has attracted much interest because of its potential to generate economic rewards and green benefits. Heteropolyacids (HPAs) are insoluble in non-polar solvents and therefore, can be used as green solid acids to replace enviromentally unsafe traditional acid catalysts such as H_2SO_4 and HF [1,2].

In this study, 12-tungstophosphoric acid (HPW) and its cesium salts $Cs_xH_{3-x}PW_{12}O_{40}$ (x=1, 2, 2.25 and 2.5) were doped with palladium and supported on mesoporous silica molecular sieve SBA-15. The as-prepared catalysts were characterized by various techniques including thermogravimetric analysis (TG-DTA), FT-IR spectroscopy, X-ray diffraction, scanning electron microscopy (SEM) and BET.

The conversion of ethanol (Et-OH) into ethylene (ET) and diethyl ether (DEE) was investigated in a temperature range of 200-350 ^oC. The ET was the main product at high temperatures while DEE was formed at lower temperatures. The results show that higher catalytic activity, characterized by conversion and selectivity, can be achieve at optimal temperature in the range 275-300 °C.

One of the major problems is the loss of catalytic activity with time on stream due to deactivation processes at 300 °C. The formation of coke deposit cause poisoning and/or pore blockage of active sites [3]. The amount of coke precursor present in the catalysts was calculated by the difference between the initial mass of spent catalyst sample after isothermal heating at 300 °C (temperature of reaction test) and the sample mass heated in nitrogen at 650 °C. Soft coke is removed from the samples through volatilization in inert nitrogen and refers to high molecular weight aliphatic oligomers. The amount of hard coke present in the catalysts was calculated as the difference between samples mass heated in nitrogen at 650 °C and mass loss of sample at 650 °C in air, when the coke was burnt out. Hard coke refers to heavy polynuclear aromatics. The sum of coke precursor and hard coke represent the total coke.

The catalytic tests demonstrate that by adding the palladium there are no significant changes to the catalytic activity and coke formation of pure heteropoly compounds. By supporting the HPW and PdPW on mesoporous molecular sieve SBA-15 the catalytic activity in ethanol dehydration reaction was improved. Palladium doping of HPA/SBA-15 significantly decreases the formation of coke deposit. A fairly good correlation between coke formation and catalyst acidity has been established, which demonstrates that the Brönsted acid sites play an important role in HPCs deactivation.

References

[1] M.M. Heravi, M.V. Fard, Z. Faghihi, Green Chem. Lett. Rev. 6 (2013) 282.
[2] A.M. Alsalme, P. V. Wiper, Y. Z. Khimyak, E. F. Koznevnikova, I. V. Koznevnikov. J. Catal. 276 (2010) 181.
[3] P. Forzatti, L. Lietti, Catal. Today, 52 (1999) 165.