Fe and Mn promoted tungstated zirconia solid acid catalysts

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Introduction

Heterogeneous catalysis is an attractive alternative to the classical technologies used for biofuels production. Solid acid catalysts, in particular are of interest for the petrochemical applications. Among them, the most investigated ones are the sulphated and tungstated zirconias. A large number of studies have been carried out trying to correlate the physical characteristics, which were controlled through the preparative method, with their catalytic activity.

Addition of dopants proved to offer the advantage of increasing the number of acidic sites and stability of the catalysts [1, 2]. Researches proved that the promotional effect on sulphated zirconia decreases as follows: Mn > Fe >> Co >> Ni > Zn [3].

The work proposed here investigates the effect of Mn and Fe dopant onto the acidic characteristics of the tungstated product. Different preparative procedures were involved and the structural characteristics evaluated.

Materials and Methods

All the preparative methods used for this work are proprietary to MEL Chemicals.

As analytic tools, XRD was used for phase analysis and stability of the products at different temperatures, N_2 adsorption/desorption was used for evaluating the surface area and porosity of the products, XRF was used for elemental analysis and NH_3 – TPD was used to look at the total acidity.

Results and Discussion

Several samples have been prepared using three different protocols and some characteristics are included in the table below:

Table 1. Composition, SA_{BET} and porosity characteristics of the prepared samples.

	Preparative method	Theoretical composition			Fresh SA_{BET} (m^2/g)	Fresh porosity (cm^3/g)
		MnO_2 (wt%)	Fe_2O_3 (wt%)	WO_3 (wt%)		
Sample 1	Method A	-	1	10	260	0.48
Sample 2	Method A	2.5	-	10	230	0.52
Sample 3	Method B	-	1	10	240	0.37
Sample 4	Method B	2.5	-	10	270	0.3
Sample 5	Method C	-	1	10	310	0.73
Sample 6	Method C	2.5	-	10	300	0.72

Method C has been chosen as comparison. The data presented in Table 1 indicate that materials with developed porosities and surface areas can be prepared by either of the routes. If method C seems to give some advantages for fresh and low and high temperature calcined materials, any of the other two methods also give reasonably thermally stable materials. Further investigations have been done looking at the evolution of the XRD fingerprinting over the 120-800ºC temperature range.

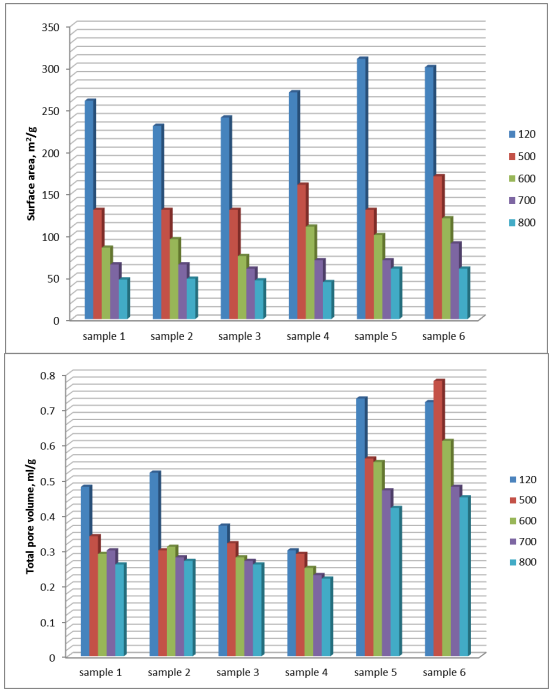

Figure 1. Surface area and porosity variation with the calcination temperature.

Significance

Tungstated zirconia is a well-known acid type catalyst which offers certain practical advantages when compared to sulphate-zirconia. The ability to produce high acidity zirconium catalysts combined with improved thermostability is investigated in this work by looking at the effect of Mn and Fe promoters.

References

1. Tabora, J.E.; Davis, R. J. *Journal of Catalysis* **1996**, *162*, 125.
2. Moreno, J. A.; Concelet, J. *Applied Catalysis A* **2001**, *210*, 151.
3. Lange, F. C.; Cheung, T. -K.; Gates, B.C. *Catalysis Letters* **1996,** *41*, 95.