

Influence of the initial form of the support on the structure, acidity and catalytic activity of WO_x-Titania catalysts

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Introduction

Since the pioneering work of Hino and Arata [1,2], tungstated zirconias have been considered active for n-alkane isomerization only when obtained by impregnation of an amorphous support. Catalysts synthesized from a crystallized zirconia were essentially inactive. We have recently shown [3] that the structure, the acidity and the catalytic activity of these catalysts were not significantly affected by the initial state of the support, Zr oxyhydroxide (amorphous) or crystallized (mainly tetragonal) zirconia. The results suggest that the reported influence of the crystalline nature of the support is due to its presence in monoclinic form. The objective of the present work was to extend the study to the corresponding titania-based system. Specifically, it seeks to determine the eventual influence of the initial form of the support (amorphous Ti-oxyhydroxide or crystalline titania in anatase form) of WO_x/TiO₂ catalysts on the surface structure, acidity and activity for two types of reactions: alcohol dehydration and alkane isomerization.

Materials and Methods

Two series of WO_x/TiO₂ catalysts, containing W surface densities up to 4.4 at. W/nm², were prepared by pore volume impregnation of two different supports; amorphous titanium oxyhydroxide (*120W series*) or titanium oxide crystallized in anatase form (*500W series*). The texture and structure of the catalysts were investigated by BET measurements, X ray diffraction (XRD), Raman and infrared spectroscopy. The catalytic activity was tested for isopropanol dehydration and n-hexane isomerization.

Results and Discussion

For a given W surface density, XRD and Raman results showed that, the crystalline composition of the support and the nature of the W species of solids of both series were similar. W, in all catalysts, was present as a surface phase. For both series, IR results indicated the presence of the band characteristic of ν(W=O) vibration and attributed to surface mono-oxo tungstate species. The envelope indicates the presence of two bands located at 1016 and 1020 cm⁻¹ attributed to highly polymerised species. The area of these bands develops respectively above a threshold of 1.3 at.W/nm² and 3.6 at.W/nm². For the two series, lutidine adsorption results, followed by IR spectroscopy, showed that Brønsted acid sites were only present for high W surface density (above 1.3 at.W/nm²). For both catalytic tests, the activity, for a given W surface density, was little affected by the initial form of the support. A minimum of W surface density, 1.3 at.W/nm² for isopropanol dehydration and 3.6 at.W/nm² for n-hexane isomerization (figure 1), appears to be required for the development of activity. The shift, in the W threshold, was attributed to the more demanding character of the latter reaction. The abundance of Brønsted acid sites (figure 2) was correlated with the sum of the area of the

infrared bands (located at 1016 +1020 cm⁻¹) characteristic of the polymerised W species and with isopropanol dehydration activity. A direct relation between activity, for n-hexane isomerization reaction, and the area of the IR band located at 1020 cm⁻¹ attributed to the most polymerised W species, was also found.

The overall results clearly showed that catalysts obtained by impregnation of amorphous titanium oxyhydroxide or titania in anatase form exhibited similar surface structure, acidity and catalytic activity. Thus, no significant effect of the initial form of the support (Ti oxyhydroxide versus anatase titanium oxide) on the development of the surface structure and catalytic properties was evidenced.

Significance

Tungstated zirconia system is often considered as a promising alternative to less environmentally friendly sulphated zirconia. It is thus of interest to investigate the influence of various preparation parameters on its properties. The present work and our previous results [3] show that for tungstated systems, the initial form of the support (amorphous oxyhydroxide or crystallized oxide) does not influence the structure, acidity and catalytic activity for two reactions (propanol dehydration and n-hexane isomerization). In addition, acidity and catalytic activity were correlated with the development of polymerised W species.

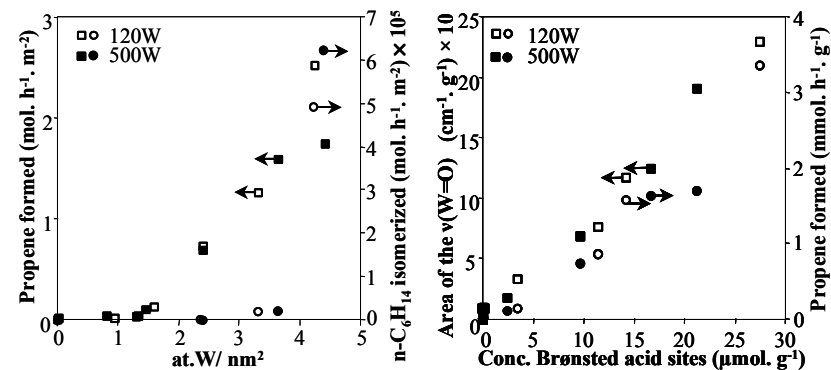


Figure 1: Initial rate of propene formation at T= 403K and D= 60 mL. min⁻¹ (left axis: squares) and Initial rate of n-hexane isomerization at 523K and P(H₂)=10³ KPa (right axis: circles) vs. W surface density.

Figure 2: Correlation between i) the sum of the area of the two infrared bands located at 1016 +1020 cm⁻¹ (left: squares) ii) the initial rate of propene formation (right: circles) and Brønsted acid sites concentration measured after lutidine desorption at 573K.

References

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