

Identification of the role of carbon in highly active and selective MoO_x-based catalysts for the skeletal hydroisomerisation of alkanes: a TPO and TAP study.

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Introduction

Catalysts based on molybdena (MoO₃) reduced at mild temperatures, e.g. 623 K, are active for the hydroisomerisation of C₄-C₇ alkanes [1-8]. These materials can be more selective than zeolite-supported platinum [2], are more resistant to sulfur and nitrogen poisoning and do not catalyse the formation of significant levels of aromatics. Further catalyst development has been hampered by the structural complexity of the material and by contradictory statements regarding the mechanism of reaction [6]. Some authors have proposed that the active phase consists of molybdenum containing some carbon (e.g. as an oxycarbides [2,7,8]), based on the fact that an induction period is needed to observe some activity when starting from fresh MoO₃ and that the uptake of carbon by the catalyst is significant. Others have proposed that the catalysis occurs on a reduced MoO_x phase [3,4], based on the fact that the MoO₃ pre-reduced in H₂ is immediately active for isomerisation upon alkane introduction. However, carbonaceous deposits are formed almost instantaneously under reaction conditions over reforming catalysts, and the carbon can thereafter be readily incorporated into the surface/bulk of the MoO_x material to form an interstitial compound [8]. These observations stress that it is difficult to answer whether or not carbon is needed for the activity of the reduced MoO_x. We report here a detailed investigation of the effect of the presence and concentration of carbon in a MoO₃-derived catalyst

Materials and Methods

The catalytic activity was measured at 623K, at a total pressure of 1 bar using a micro-pilot. Gas samples were analysed by gas chromatograph (Perkin-Elmer Clarus 500). The Temperature Programmed Oxidation (TPO) experiments were carried out in the same reactor using on-line FTIR analyser to detect the CO₂ evolved. The TAP (temporal analysis of product) reactor was packed with 30 mg of molybdenum oxide catalyst in a thin-zone manner. After catalyst reduction at 623 K, an Ar/H₂/Butane mixture (1/1/1) was repeatedly pulsed over the reduced catalyst at the same temperature. In order to deconvolute the butane and isobutene contributions, the major fragments of butane and isobutane were monitored in a preliminary experiment over inert particles.

Results and Discussion

During the atmospheric pressure experiments, the selectivity to isobutane was higher than 95%. The sample was run under the butane feed for 10, 100 or 600 min before a TPO was carried out to determine the amount of carbon present over the catalyst. The isobutane yield appeared to be independent of the carbon-content, at least over the range of concentrations obtained here (Figure 1). The TAP reactor allowed us probing the reactivity of the reduced oxides prepared under H₂ by sending small pulses of butane (3 orders of magnitude

smaller than the number of surface Mo) on the sample, that only gradually modify the surface. During the TAP experiment, the n-butane conversion decreased with the number of pulses, while the yield of isobutene remained constant at a significantly lower level. This suggests that an extensive deposition of carbonaceous deposits or carbonization of the sample was taking place. Figure 2 reports the butane conversion and isobutene yield as a function of the amount of carbon deposited on the catalyst, this result strongly suggests that the carbon uptake and related modifications of the catalysts have no significant effect on the active phase. The moment analysis of the n-butane multipulse responses showed that the n-butane adsorption constant decreased while the desorption constant did not change upon increased exposure to the n-butane/H₂/Ar pulses. The butane transformation constant also showed a small variation.

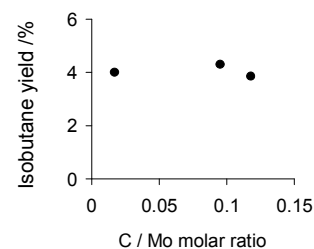


Figure 1: Isobutane yield for the reduced MoO₃ as a function of the uptake of carbon determined by TPO. T = 623 K, feed = 10% n-butane in H₂.

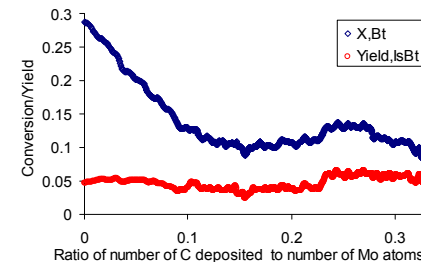


Figure 2: TAP data showing the evolution of the conversion of n-butane (X,Bt) and the yield to isobutane (Yield, IsBt) as a function of C/Mo ratio. T = 623 K

Significance

A series of temperature-programmed oxidation (TPO) and temporal analysis of product (TAP) experiments showed that the oxycarbide carbon content of molybdenum oxide-based phases is not related to the activity of the sample for the skeletal isomerization of n-butane. While the TAP data demonstrated marked changes in the adsorption properties of the sample due to varying exposure of the pre-reduced MoO₃ sample to the butane-containing feed, the isobutane yield remained essentially constant.

References

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