SBA-1 supported tungsten and molybdenum oxide-based catalysts for propylene metathesis

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Abstract: SBA-1 supported tungsten and molybdenum oxide-based catalysts were prepared by incipient wetness impregnation method. The catalysts were characterized with different physicochemical techniques and tested in propylene metathesis. The effect of high temperature activation (550-700 °C) with inert gas (argon) and propylene on the activity was investigated. In both series of catalysts the metathesis activity rises with the decrease of the metal oxide loading. Moreover, significant effect of the short-time high temperature activation with propylene was observed.

Keywords: Metathesis, Alkenes, Activation.

1. Introduction

Tungsten and molybdenum oxide-based catalysts supported on oxide supports like SiO_2 or γ-Al_2O_3 are widely applied in industrial metathesis of alkenes due to the low price and simplicity of the preparation. Both catalysts need high-temperature activation, typically in an inert gas, before olefin metathesis starts[1,2]. To shorten the induction period of the metathesis process, pretreatment of the catalyst with olefins in moderate temperature or its photoreduction with carbon monoxide were proposed[3,4]. The recent report reveals that the high temperature pretreatment of MoO_3/SiO_2 or WO_3/SiO_2 catalysts with propylene leads to remarkable (100-1000 fold) increase of their activity in propylene metathesis[5]. Such simply pretreated materials exhibit metathesis activity (calculated per metal atom) as good as the catalysts based on organometallic precursors, prepared in much more complex and expensive ways.

The high metathesis activity is connected typically with the presence of dispersed molybdenum and tungsten species. In the case of MoO_3/SiO_2 and WO_3/SiO_2 catalysts, the activity is probably correlated with the content of monomeric $Mo(=O)_2$ sites[,6]. The concentration of this species can depend strongly on the metal loading, preparation conditions and the precursors applied. The porosity of the support is also an important factor. The high specific surface area of the support provides more adsorption sites that may stabilize the dispersed species.

Considering the above, the results concerning metathesis activity of tungsten and molybdenum oxide-based materials supported on SBA-1 with the cubic mesopore architecture (space group pm3n) and high specific surface area ($S_{BET} = 1181\ m^2g^{-1}$) are presented here. The effect of the high temperature pretreatment at various conditions is discussed as well.

2. Experimental

Two series of catalysts with 1, 3, 5, 10 and 20 wt.% of Mo and W supported on mesoporous silica SBA-1 were obtained by the incipient wetness method of preparation. Pure SBA-1 were prepared according to the procedures described elsewhere[7.] All prepared materials were characterized with different physicochemical techniques (low temperature adsorption-desorption, SEM-TEM, XRD, XPS, TPR and TPD). Catalytic performance in propylene metathesis was tested using the continuous method with a quartz tubular-type flow reactor at 50 or 250 °C. Before the catalytic tests the samples were activated in the inert gas (argon) or in propylene in the temperature range between 550 and 700 °C.

3. Results and discussion

In both series of the catalysts, the activity in propylene metathesis varies strongly with the activation conditions and metal loading. The specific activity (calculated per mol of Mo or W) rises with the decrease of the metal content, confirming that the dispersion of the metal species is crucial for alkene metathesis. Additionally, the effect of the activation method was investigated for samples containing 20 wt.% Mo or W. The catalysts pretreated in argon (120 min, $V_{total} = 20$ cm^3/min) in temperatures 550-700 °C exhibit minor activity. However, for both series of the catalysts, the activity rises with the increase of the activation temperature. Short high temperature activation of the catalysts in propylene (15 min, $V_{total} = 20$ cm^3/min) brings a significant rise of the activity. Figure 1 summaries the results obtained for the catalysts activated in argon and propylene.

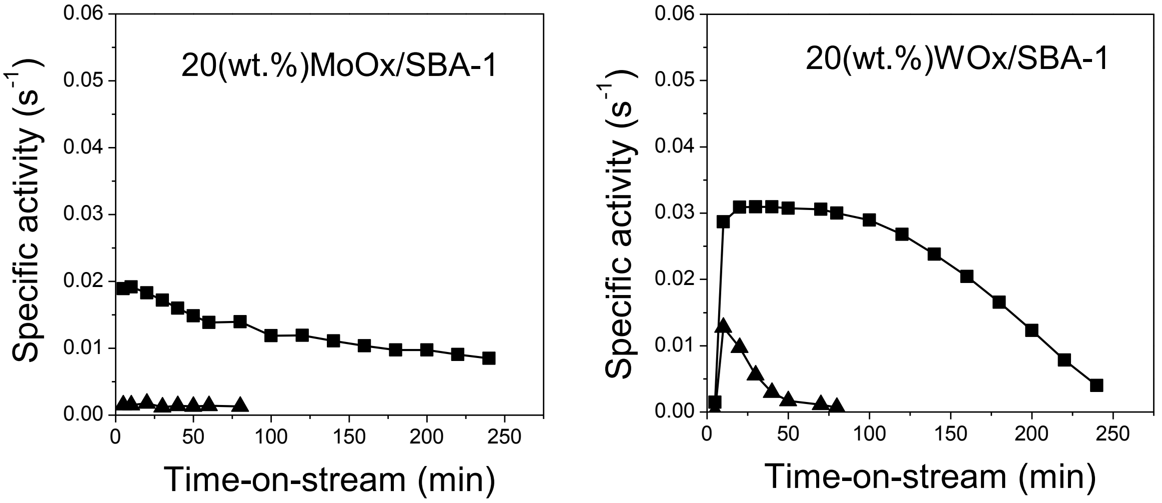

Figure 1. Metathesis activity of samples with 20 wt % of Mo and W supported on SBA-1 after activation in argon and propylene. Reaction conditions: Temperature 50 °C (for Mo-based catalyst) and 250 °C (for W-based catalyst); $m_{cat} = 200$ mg, $V_{C3H6} = 28$ cm^3/min. Activation conditions: 120 min at 650 °C in dray and deoxygenated argon 20 cm^3/min (▲) or 15 min at 650 °C in propylene/argon mixture 5/15 cm^3/min (■).

In the case of the molybdenum oxide-based catalyst activated with propylene at high temperature, a very short induction period (about 10 min) was observed during the metathesis process and the activity drops gradually with the time-on-stream. The tungsten-based catalyst after a short induction period (about … min) works stable a longer time, compared to the molybdenum one, but the catalytic activity decreased quite rapidly then.

4. Conclusions

Simple incipient wetness impregnation of mesoporous silica with the high surface area and suitable procedures of activation with propylene leads to highly active in propylene metathesis tungsten and molybdenum oxide-based catalysts. The temperatures above 650 and 550 °C are required for the short-time propylene activation of the tungsten and molybdenum catalysts, respectively.

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