

Genesis of acid-base support properties with variation of preparation conditions: cumene cracking and its kinetics

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Abstract

Si-Al, Si-Ti and Si-Mg supports were synthesized by sol-gel method and evaluated in the cumene reaction. Acid-base properties of the supports those were determined by using 2-propanol reaction into propene and acetone, which allow to know quantitatively the support properties. The supported catalysts were prepared with NiMo, NiW and CoMo by the incipient wetness method. In addition, the supported catalysts were evaluated for cumene cracking and its kinetic parameters were obtained by applying the Langmuir-Hinshelwood model. The activation energy was 27.75 kcal mol⁻¹ and the heat of absorption calculated with the Van't Hoff equation was 14.15 kcal mol⁻¹. Si-Al supported NiMo catalyst were found more active in cumene cracking most probably due to its stronger acidity generated during the support preparation.

Introduction

The demand for stringent environmental regulations or clean fuel is attracting attention of researcher as well as refiners to hydrotreating of various petroleum fractions using new catalytic materials and the development of new and more efficient process. Therefore, the use of mixed oxides (SiO₂-Al₂O₃, SiO₂-MgO, SiO₂-TiO₂) as supports results to be very attractive with respect to their textural properties and interaction with the active metals. Apart from that sol-gel method is convenient to prepare supports and hetero-poly-condensation of different metals is responsible to form strong bonds between metal-O-Si (M-O-Si), which controls the support particle size and distribution of the metal particles in solid matrix [1]. Cumene cracking is one of the most important parameter to confirm acidity of the support as well as catalysts; however, it has been reported that the acidity of sulfided catalyst is modified during the sulfidation of the supported catalysts [2].

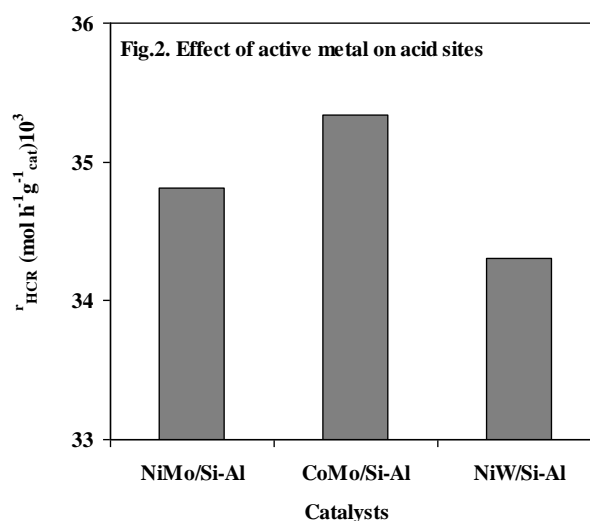
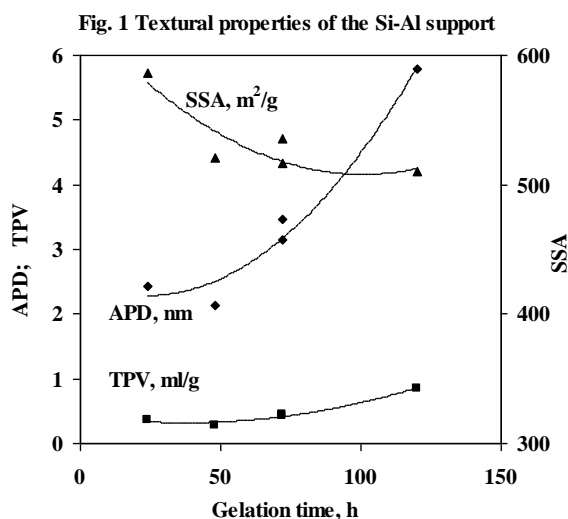
Experimental

Different supports of mixed oxides were prepared (SiO₂-MgO, SiO₂-Al₂O₃, SiO₂-ZrO₂, SiO₂-TiO₂) by means of the sol-gel method with varying the gelation time, precursor molar ratios etc. Catalysts were prepared with NiMo, NiW and CoMo salts using incipient wetness impregnation method. Supports and catalysts were characterized to obtain BET SSA, PV and APD in a Quantachrome Nova 4000 with using nitrogen at -196°C. The promoted catalysts sulfided *in situ* with a mixture of CS₂+H₂ at 400°C for 3 h and were evaluated at atmospheric pressure in a tubular micro-reactor for cumene cracking in the range of 300-400°C during 4 h. Products were analyzed with an on-line system gas chromatography. The catalyst (NiMo/AlSi) is employed to obtain the kinetic parameters at low conversion using Langmuir-Hinshelwood model.

Results and discussion

Fig. 1 shows the textural properties of the supports, which vary as function of the gelation time. In general, it can be observed that average pore diameter (APD) and total pore volume (TPV) increase with increasing the gelation time while specific surface area (SSA) showed decreasing tendency which suggests

that there is a reduction of the sample volume during the phase separation in the sol-gel media. However, decrease in surface is relatively lesser than the effect shown for pore volume and pore size grows as the time advances most likely due to the M-O-Si cross-linking.



In order to see these preparation methods on the genesis of acid base properties supports were tested against cumene cracking and the results are shown in **Table 1**. The number at the end of the support type

Table 1. Evaluation of supports

Supports	$r_{HCR} (\text{mol h}^{-1} \text{g}_{cat}^{-1}) 10^3$
MgSi-24	0.0
ZrSi-72	0.12
Si-Zr48	12.2
AlSi-48	1.9
AlSi-72	184

indicates the gelation time to prepare each support. It can be seen from the table that Si-Mg do not exhibit cracking activity and a possible explanation is the basicity that Mg gives to the support. An activity variation for Si-Zr supports is observed with variation of preparation conditions, which confirms the different interaction of Zr and Si atoms. The low conversion for Si-Zr is reported in several literatures such as Nahas et al. [3] who showed 24 % at 400 °C. In contrast the SiO₂-Al₂O₃ shows a very high conversion at 400 °C due to its strong Brønsted

acidity [1]. The effect of catalyst active metal for cumene cracking is shown in **Fig. 2**, where CoMo showed better synergy for the Brønsted acid sites over Si-Al support.

The activation energy and heat of adsorption is also determined for NiMo/Si-Al supported catalyst, which is reported in **Table 2**. The cumene cracking reaction was carried out in micro-flow reactor at atmospheric pressures, which was operated under differential regime (up to 15% conversion). Langmuir-Hinshelwood kinetics was used for obtaining kinetic parameter considering that only cumene is absorbed on an active site. In addition, heat of adsorption for cumene on sulfided active sites was calculated, which are in agreement with those reported in literature [4]. In conclusion, mixed oxides have good catalytic activity in different reactions and promoters and active metal give them the desired behavior.

Table 2. Kinetic parameters

A	9.5×10^7
$E_A, \text{kcal mol}^{-1}$	27.75
$\Delta H, \text{kcal mol}^{-1}$	-14.15

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