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## Oligomerization of propene over ZSM-5 modified with Cr and W

## Oligomerización de propeno usando como catalizador ZSM-5 modificada con Cr y W

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### Abstract

In this paper, the composition of ZSM-5 was modified with Cr and W by impregnation, isomorphous substitution and ion exchange, and the resulting catalysts were evaluated in the oligomerization of propene.

----- **Keywords:** Oligomerization, olefine, ZSM-5, diesel, heterogeneous catalysis

### Resumen

En el presente trabajo se modificó la composición de la ZSM-5 con Cr y W por impregnación, sustitución isomórfica e intercambio iónico, y los catalizadores resultantes se evaluaron en la oligomerización de propeno.

----- **Palabras clave:** Oligomerización, olefina, ZSM-5, diesel, catálisis heterogénea

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## Introduction

World-Wide demand of Diesel has increased 30% in last years, due to its low cost and better performance compared with gasoline; in Colombia it is estimated that demand of diesel will double in the next 10 years. Due to these reasons, fuel production alternatives are sought in order to fulfill environmental legislation and meet growing demand with technologies developed in the country [1]. One of these alternatives is oligomerization of light olefins [2].

This oligomerization reaction is carried out in the presence of an acid catalyst, and consists of two steps, propagation (chain growth), and elimination. Then the olefins combine with each other forming dimers, trimers, tetramers and even higher oligomers. The oligomerization reactions are not elementary and are often accompanied by various parallel reactions. In addition to oligomers, aromatics, coke and saturates are often formed, which is indicative of the occurrence of cracking, isomerization, dehydrocyclization, methyl and hydrogen transfer even at low temperatures. The product spectrum is influenced by both the nature of the catalyst and the reaction conditions [1].

Many zeolites and related materials have been used as catalysts in this reaction. The most widely used are shape-selective medium-pore zeolites that decrease the quantity of branched oligomers [1]; pentasil-type zeolites, like ZSM-5, are classified in this pore range. Also these zeolites were modified with other metals by ion exchange, impregnation and isomorphous substitution to improve its selectivity to distillate-range products [2-4].

High conversions were obtained when these materials are used as catalysts, but selectivity toward distillate-range products was lower than 50% [5]. Catalysts like titanium oxides, mesoporous and other amorphous materials, modified with Cr and W have shown higher selectivity, around 80%, but more branched oligomers were obtained with lower cetane index [6,7]. In this paper, ZSM-5 modified with Cr and W as catalyst in propene oligomerization at 270 °C and 2.5 MPa was investigated. Highest

conversion was around 70%, and selectivity toward hydrocarbons C6-C10 was close to 60%.

## Experimental

8 catalysts were prepared using hydrothermal synthesis from silica and alumina which were obtained previously in the laboratory. Table 1 shows the synthesis gel molar compositions and the theoretical percentages of Cr and W for the catalysts. The procedure for the synthesis of Na-ZSM-5 was previously reported [8]; its proton form was produced by three consecutive ion exchanges with fresh water solutions 0.2 M of  $\text{NH}_4\text{NO}_3$  (MERCK 98%) for 3 hours at 50°C each exchange to obtain  $\text{NH}_4$ -ZSM-5. Then, part of this solid was calcined at 550°C for 6 hours to obtain H-ZSM-5.

Cr-H-ZSM-5(i) was prepared from  $\text{NH}_4$ -ZSM-5 by ion exchange with a water solution 0.02 M of  $\text{Cr}(\text{NO}_3)_3$  (MERCK 98%) for 6 hours at room temperature, then the solid was calcined at 550°C for 6 hours. W-H-ZSM-5(1), W-H-ZSM-5(2), W-H-ZSM-5(3) were prepared by impregnation of  $\text{NH}_4$ -ZSM-5 with the quantity of  $(\text{NH}_4)_6\text{W}_{12}\text{O}_{36}$  needed to achieve 1, 2 and 3% of W in final catalysts. Solids were calcined at 550°C for 6 hours. Cr-H-ZSM-5(0.5), Cr-H-ZSM-5(1), Cr-H-ZSM-5(2) were prepared by isomorphous substitution of Cr with the synthesis gel molar compositions showed in table 1. The procedure was similar to that described above for ZSM-5.

X-ray diffraction (XRD) patterns were obtained on a Rigaku Miniflex instrument with a Cu source ( $\lambda=1,5418 \text{ \AA}$ ), operated at 40 kV and 30 mA. The concentration of Na was determined by atomic absorption spectroscopy (AA) (Thermo Electron Corporation S Series equipment), and the composition of other compounds were determined by X-ray fluorescence spectroscopy (Philips Magix Pro). Specific surface area (SSA) and porosity characteristics were determined by nitrogen sorption isothermally at -196°C using a Micromeritics ASAP 2020 instrument. The acidic properties of some samples were tested by temperature programmed desorption (TPD)

of ammonia carried out on a Micromeritics TPD/TPR 2900 instrument with a thermal conductivity detector (TCD). The FT-IR spectra of catalysts were recorded using Infinity Gold Mattson infrared spectrophotometer in the range 2100-700  $\text{cm}^{-1}$  on thin wafers of KBr in which

dispersed zeolite was 1 wt%. The Raman spectra were obtained by using the dispersive technique on a LabRam Jobin-Ivon triple-monochromator spectrometer using laser lines (wavenumbers 514, 632 nm y 785 nm) and a CDD detector cooled by Peltier effect.

**Table 1** Catalysts synthesis gel molar composition and theoretical percentage of Cr and W

<i>Catalyst</i>	<i>Synthesis gel molar composition</i>	<i>%*</i>	<i>Metal</i>
H-ZSM-5	5.2 $\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:117 \text{ SiO}_2:6.3 \text{ TPABr}:2,275.2 \text{ H}_2\text{O}$	---	---
<i>Ion Exchange</i>			
Cr-H-ZSM-5 (i)	5.2 $\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:117 \text{ SiO}_2:6.3 \text{ TPABr}:2,275.2 \text{ H}_2\text{O}$	---	Cr
<i>Impregnation</i>			
W-H-ZSM-5 (1)	5.2 $\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:117 \text{ SiO}_2:6.3 \text{ TPABr}:2,275.2 \text{ H}_2\text{O}$	1	W
W-H-ZSM-5 (2)	5.2 $\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:117 \text{ SiO}_2:6.3 \text{ TPABr}:2,275.2 \text{ H}_2\text{O}$	2	W
W-H-ZSM-5 (3)	5.2 $\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:117 \text{ SiO}_2:6.3 \text{ TPABr}:2,275.2 \text{ H}_2\text{O}$	3	W
<i>Isomorphous substitution</i>			
Cr-H-ZSM-5 (0.5)	5.2 $\text{Na}_2\text{O}:0.6\text{CrO}_3:\text{Al}_2\text{O}_3:116.7\text{SiO}_2:6.3\text{TPABr}:2,275.2\text{H}_2\text{O}$	0.5	Cr
Cr-H-ZSM-5 (1)	5.2 $\text{Na}_2\text{O}:1.2\text{CrO}_3:\text{Al}_2\text{O}_3:116.7\text{SiO}_2:6.3\text{TPABr}:2,275.2\text{H}_2\text{O}$	1	Cr
Cr-H-ZSM-5 (2)	5.2 $\text{Na}_2\text{O}:2.3\text{CrO}_3:\text{Al}_2\text{O}_3:116.7\text{SiO}_2:6.3\text{TPABr}:2,275.2\text{H}_2\text{O}$	2	Cr

Catalysts were used in the form of cylindrical extrudates of 0.2 x 0.5 cm with 40 % of zeolite and 60% of binder (Seudobohemite Versal la Roche 200 or kaolin). Oligomerization reactions were carried out in a stainless steel tubular reactor of 1 cm diameter with temperature, pressure, and mass flow controls. All products were analyzed on-line by a gas chromatograph Agilent 6890 equipped with FID and mass detectors and a HP-1MS capillary column (60m x 0.25mm x 0.25mm). The reactant mixture contained 5% of propene in  $\text{N}_2$  (44 mL/min). Experiments were carried out at 270°C and 2.5 MPa with 1 g of catalysts.

## Results and discussion

XRD patterns of catalysts are shown in figure 1, materials with high crystallinity can be observed without crystalline impurities, which are in agreement with previous reports for ZSM-5 [9]. Catalysts prepared by isomorphous substitution of Cr showed the greatest crystallinity. Usually the peak at 7.8° has higher intensity than the one at 8.7°, but in this study the peak at 8.7° became the highest with Cr modifications.

Table 2 presents the chemical composition of catalysts along with the Na loading before and after  $\text{NH}_4^+$  ion exchange processes. As can be observed

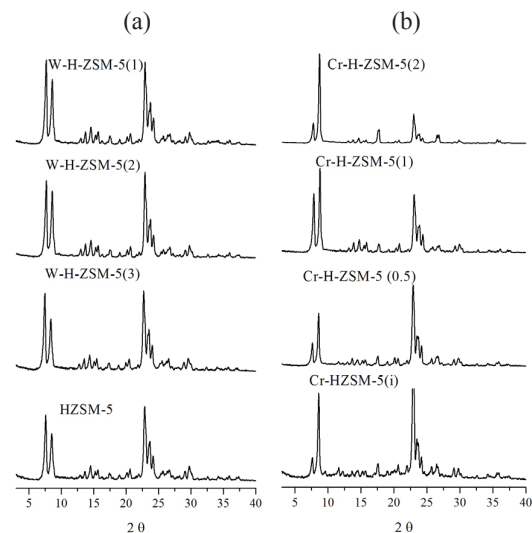
the final content of Na was low for all catalysts which is important since the oligomerization reaction requires zeolites with high acidity and low steric hindrances [1]. Catalysts prepared by isomorphous substitution of Cr showed less Al than the other ones, which means that Si/Al molar ratio increased and the number of acid sites decreased, besides this could cause the increase in crystallinity of these catalysts. Impregnation processes were inefficient and W final percentages were lower than the expected ones (1.2 and 3%).

Table 3 depicts a comparison of specific surface area of the catalysts before and after extrusion with alumina and kaolin. The SSA decreased with Cr and W modifications probably because atoms or molecules related with these metals located on in the surfaces can block  $N_2$  adsorption in the pore structure of materials. Specific surface areas of extruded catalysts were affected by the binder employed; the obtained values were lower than the initial ones, because SSA of alumina and kaolin were 320 and 19  $m^2/g$  respectively.

**Table 2** Catalyst chemical composition

Catalyst	Na before $NH_4^+$ ion Exchange (%)	Na after $NH_4^+$ ion Exchange (%)	Al (%)	Si (%)	Cr (%)	W (%)	Si/Al
H-ZSM-5	0.65	0.009	0.71	32.35			43.66
Cr-H-ZSM-5 (i)	0.67	0.015	0.70	31.20	0.003		42.52
Cr-H-ZSM-5 (0.5)	0.43	0.037	0.31	30.80	0.04		95.19
Cr-H-ZSM-5 (1)	0.55	0.043	0.37	32.00	0.06		84.00
Cr-H-ZSM-5 (2)	0.67	0.023	0.44	31.20	0.21		68.43
W-H-ZSM-5 (1)	0.71	0.013	0.69	31.40		0.61	43.43
W-H-ZSM-5 (2)	0.63	0.019	0.69	31.20		0.93	43.40
W-H-ZSM-5 (3)	0.59	0.015	0.70	34.40		2.02	47.15

FT-IR spectra of catalysts are presented in figure 2. All spectra of the samples showed a typical ZSM-5 structure [10]. The strong absorption band at 1320  $cm^{-1}$  has been assigned to the internal vibration and the asymmetric stretching



**Figure 1** XRD patterns of catalysts (a) catalysts modified by isomorphous substitution, (b) catalysts modified by impregnation and ion exchange

of  $SiO_4$ ,  $AlO_4$  tetrahedra, which shifted to higher wavenumbers by the modifications with Cr and W; this indeed suggest the good incorporation of Cr in the framework or the presence of this metal in compensating positions, like it was previously

reported for other metal incorporations in MFI zeolites [11, 12, 13,14]. Besides, the presence of W on the surface of zeolites prepared by impregnation could show the same effect [15]. The absorption bands at 798, 972 y 1192  $\text{cm}^{-1}$  are characteristic of  $\text{SiO}_4$  tetrahedron units and correspond to the symmetric and asymmetric stretching vibration of the double rings and the linkages. The external asymmetric stretching vibration near 1192  $\text{cm}^{-1}$  was assigned to the presence of structures containing four chains of 5-membered rings arranged around a two-fold screw axis, as in the case MFI structures. The internal asymmetric stretching vibration of Si-O-T linkage was observed at 972 $\text{cm}^{-1}$ . The band near 798  $\text{cm}^{-1}$  was assigned to the symmetric

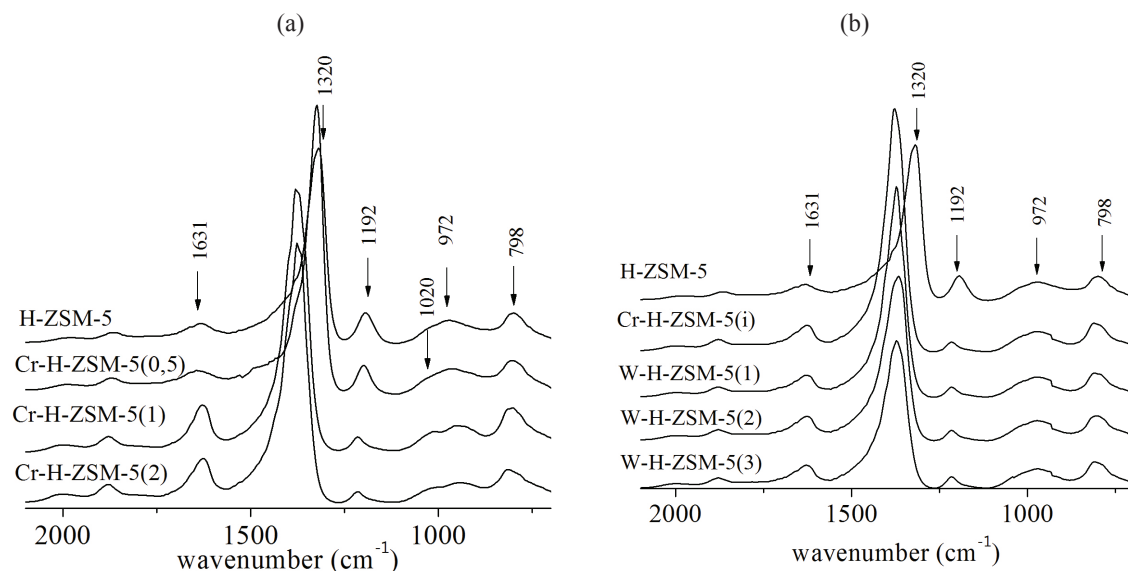
stretching of the external linkages. The band at 1631  $\text{cm}^{-1}$  was attributed to OH bending vibration [10,16]. The internal asymmetric stretching vibration of Si-O-T linkage presented at 972 and 1194  $\text{cm}^{-1}$  were observed to shift towards higher wavenumbers with the increase of the Si/Al ratio. This shift was due to the slightly lower mass of aluminum compared to that of silicon. This effect can be observed on samples where Al was replaced by Cr and with a higher Si/Al molar ratio [10]. The additional band near 1020  $\text{cm}^{-1}$  in samples prepared by isomorphous substitution of Cr suggested the presence of different linkages Si-O-T to those present in the H-ZSM-5 that could be assigned to Si-O-Cr linkages [11-13]

**Table 3** Specific surface area BET of catalysts ( $\text{m}^2/\text{g}$ )

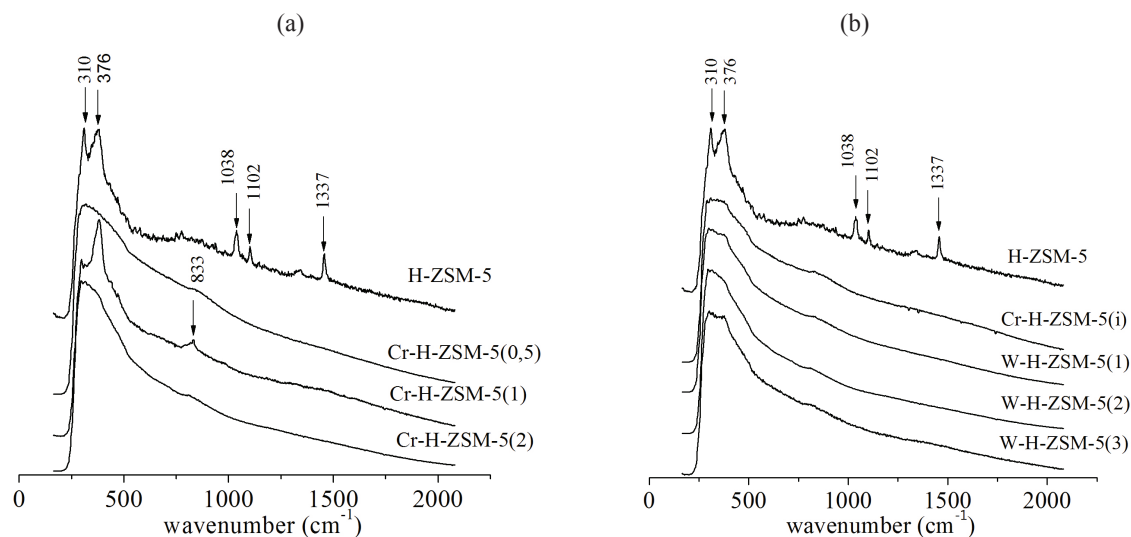
<i>Catalysts</i>	<i>Before extrusion</i>	<i>Extruded with alumina</i>	<i>Extruded with kaolin</i>
H-ZSM-5	400.92	324.33	158.44
Cr-H-ZSM-5 (i)	392.81	309.91	163.28
Cr-H-ZSM-5 (0.5)	344.21	304.50	168.96
Cr-H-ZSM-5 (1)	389.38	311.96	177.29
Cr-H-ZSM-5 (2)	365.48	315.76	128.72
W-H-ZSM-5 (1)	393.40	309.56	158.08
W-H-ZSM-5 (2)	397.54	313.95	158.72
W-H-ZSM-5 (3)	458.21	314.46	170.80

In figure 3 the Raman spectra of all catalysts with the typical bands for zeolitic materials are shown. The bands between 1000 and 1200  $\text{cm}^{-1}$  correspond to the symmetric and asymmetric stretching vibration of Si-O linkages. The bands between 300 and 500  $\text{cm}^{-1}$  are assigned to bending modes of O-Si-O and Si-O-Si linkages as well as Si-O-Si-O deformation modes. The

bands between 500 and 1000  $\text{cm}^{-1}$  are assigned to vibration modes of low intensity of tetrahedron units [17, 18]. The presence of Cr and W overlap the symmetric and asymmetric stretching vibration of Si-O linkages. A weak band at 833  $\text{cm}^{-1}$ , was insinuated in catalysts prepared by isomorphous substitution of Cr, in the range for vibration modes of tetrahedron units.



**Figure 2** FT-IR spectra of catalysts. (a) catalysts modified by isomorphous substitution, (b) catalysts modified by impregnation and ion exchange



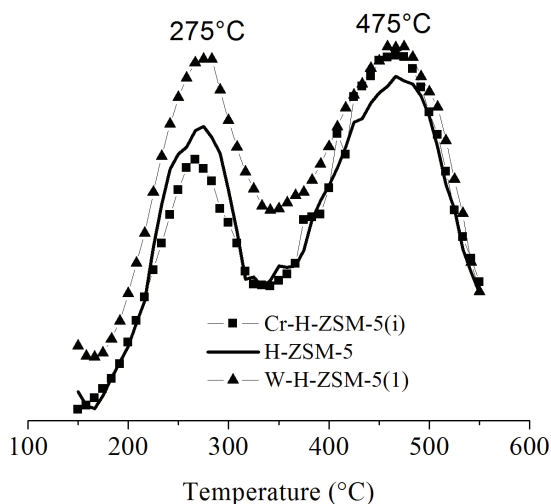
**Figure 3** Raman spectra of catalysts.(a) catalysts modified by isomorphous substitution, (b) catalysts modified by impregnation and ion exchange

Figure 4 shows a typical acid site distribution for ZSM-5 as obtained by TPD of ammonia of 3 catalysts. All samples exhibit two well resolved desorption peaks: the low-temperature peak at 200-300 °C and the high-temperature peak at

370-550 °C, that generally correspond to weak and strong acid sites, respectively [10]. The presence of Cr in the catalyst by ion exchange decreased weak acid sites and increased strong acid sites. The modification of catalysts surfaces



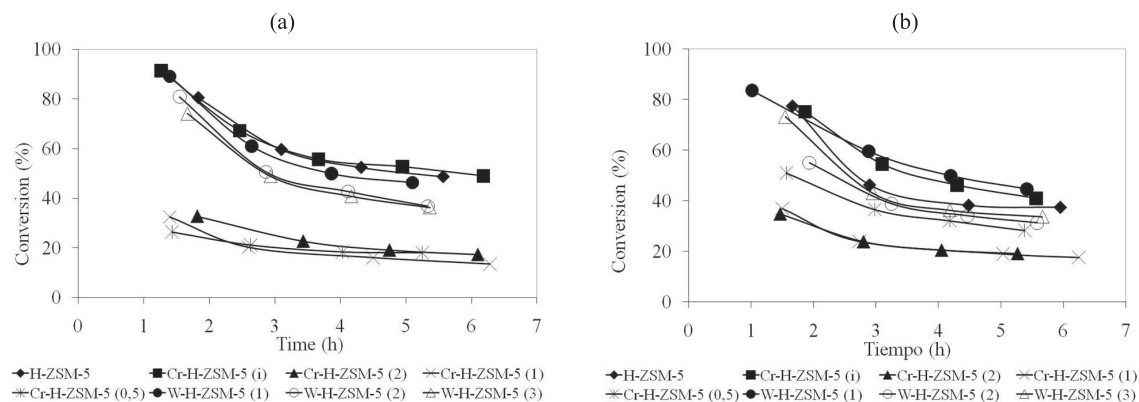
by impregnation of W increased the two kinds of acid sites. These changes in the quantity of acid sites were reflected on catalyst activity.



**Figure 4**  $\text{NH}_3$ -TPD profile of catalysts

The propene oligomerizations results are presented in figure 5. The best catalysts were

H-ZSM-5, Cr-H-ZSM-5(i) and W-H-ZSM-5(1) (48, 52 and 46 % respectively with alumina and 39.41 and 46 % with kaolin). Conversion levels decreased with isomorphous substitution of Cr, because these catalysts had less Al content and therefore less acidity. The catalyst prepared by Cr ion exchange had better performance than the H-ZSM-5 without modifications, in agreement with TPD results where the number of strong acid sites of Cr-H-ZSM-5(i) is higher. With the lowest W impregnation percentage an increase in conversion levels was achieved. Only superficial acidity was modified by impregnations, the higher impregnation levels could block access of olefins to active sites within pores. Moreover this modification decreased specific surface area of catalysts. It was not clear the effect of binder in the catalytic activity, but when alumina was used, conversion was slightly higher. All catalyst showed deactivation due coke deposition, according to thermal analysis and carbon determinations made to catalysts after reaction.



**Figure 5** Conversion of propene oligomerization with catalysts (a) extruded with alumina (b) extruded with kaolin

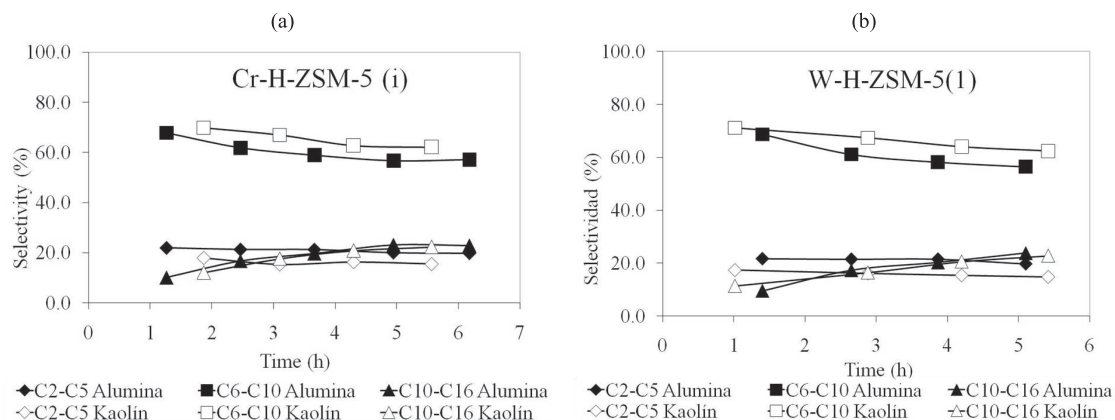
Reaction products were classified in 3 different groups according to its number of carbon atoms, C2-C5, C6-C10 and C10-C16. 95% of products were olefins with a low branched degree, only methyl radical were observed. Figure 6 shows selectivity graphs of Cr-H-ZSM-5(i) and W-H-ZSM-5(1) that were the best catalysts. All

catalysts showed higher selectivity levels to C6-C10 hydrocarbons (50-85%). Products in the range C2-C5 demonstrated the occurrence of disproportionation and cracking reactions. Products in range C10-C16 had values between 16 and 26 %, Cr-H-ZSM-5(i), Cr-H-ZSM-5(0.5) and catalysts impregnated with W increased selectivity



toward these hydrocarbons while Cr-H-ZSM-5(1) and Cr-H-ZSM-5(2) decreased selectivity toward

C2-C5 hydrocarbons. This demonstrated that the higher Cr contents enhanced cracking reactions.



**Figure 6** Selectivity of (a) Cr-H-ZSM-5(i) and (b) W-H-ZSM-5(1)

## Conclusions

8 catalysts were obtained and their correspondence with ZSM-5 was confirmed by XRD patterns, FT-IR and Raman spectra. Chemical composition of catalyst showed the high decrease of Na content achieved with ion exchange processes along with substitution of Al for Cr in zeolite frameworks of catalysts prepared by isomorphous substitution. Although the presence of Cr in framework was not confirmed, XRD patterns, FT-IR and Raman spectra showed the modification of zeolite structures, which allowed inferring that isomorphous substitution may have taken place.  $\text{NH}_3$ -TPD profiles showed the relationship between the acidity changes and the catalytic activity of catalysts with Cr and W modifications.

The results of catalytic activity in propene oligomerization showed that the performance of H-ZSM-5 was improved only with low Cr and W loadings. Oligomerization products were mostly olefins with a low branched degree. The most important products were C6-C10 hydrocarbons.

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