



NiO–W₂O₃/Al₂O₃ catalysts for the production of ecological gasoline: Effect of both NiO and the preparation method on the isobutene oligomerization selectivity

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ABSTRACT

The results obtained for the oligomerization of C₄ olefins in order to produce high octane ecological gasoline by using NiO–W₂O₃/Al₂O₃ catalysts prepared by both the wetness impregnation and sol–gel methods, are reported. High selectivity towards C₈⁼ olefins, avoiding the formation of heavier olefinic products, as well as an excellent stability were reached by means of the NiO–W₂O₃/Al₂O₃ impregnated catalyst. The characterization of the catalysts by XRD, total specific surface area and FTIR pyridine adsorption are also reported.

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1. Introduction

An attractive option to produce high octane ecological gasoline, free of pollutant components like aromatic hydrocarbons and low sulfur content is the oligomerization of the C₃–C₄ paraffin/olefin fraction of the FCC units, in order to produce iso–octene/iso–octane fractions, which after a single hydrogenation step produce gasoline with a high research octane number, RON 105 [1,2]. Typically, the catalysts used in this process are liquid acids such as phosphoric acid impregnated in solid supports [3,4]; however, the disposal of this kind of catalysts produces important pollution and the substitution of them by cleaner solid acid catalysts is a challenge around the world. In the olefin dimerization, the undesirable formation of high molecular weight oligomers provokes important deactivation problems [5]: these oligomers act as the precursors of the growth of carbonaceous slots on the catalyst surface, leading to the deactivation process [6–11]. The design of new catalysts for this reaction is then focused on reaching the highest selectivity towards C₈⁼ olefins, avoiding the formation of heavier olefinic products (+C₁₂⁼). Some of the developed solid acid catalysts include: Ziegler–Natta-based catalysts [12], benzyl sulfonic acid on silica [13], zeolites [14,15], montmorillonite [16], zirconium oxide [17], sulfated titania [6,7] and sulfated zirconia [18,19]; however,

low selectivity to the dimer and deactivation problems remain in all of them. According to the afore mentioned, it has been recently reported that the addition of NiO to sulfated ZrO₂ increases the stability and selectivity towards the C₈⁼ fraction, drastically diminishing the formation of C₁₂⁼ and heavier olefins in the isobutene oligomerization [20]. Looking for an improved solid acid catalyst, in the present work NiO–W₂O₃/Al₂O₃ catalysts were prepared by the impregnation and sol–gel methods, since it has been reported that W₂O₃ is an important solid acid catalyst [21–23] and NiO improves the selectivity of the reaction towards lower molecular weight olefinic fractions [20]. The catalysts were characterized by N₂ adsorption, XRD, and FTIR pyridine adsorption; evaluated in the isobutene oligomerization reaction.

2. Experimental

2.1. Preparation of catalysts

The γ-alumina support prepared by the sol–gel method was obtained following the general procedure reported by Deng et al. [24]: 1.2 g of cetyl tert-butyl ammonium (CTBA) were mixed with 150 mL of a butanol/water solution (ratio 30:70, v/v) at 60 °C with vigorous stirring and reflux until a homogeneous mixture was obtained. Then, 6.0 g of the aluminum precursor (aluminum sec-butoxide) were added. The resulting solution was gelled with an ammonium hydroxide solution in order to maintain pH 9. The solution was kept under stirring for 24 h. After gelling, the solid

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Table 1
Textural properties and acidity for the NiO–W₂O₃/Al₂O₃ catalysts.

Sample	NiO W ₂ O ₃ (wt%) ^a	Specific surface area (m ² /g)	Pore diameter (nm)	Acidity ^b (μmol/g)	Acidity ^b (μmol/m ²)
Al ₂ O ₃		344	8.9	109	0.31
W ₂ O ₃ /Al ₂ O ₃ -SG	19.1	345	8.0	170	0.49
NiO–W ₂ O ₃ /Al ₂ O ₃ -SG	4.4 18.3	121	5.0	223	1.84
NiO–W ₂ O ₃ /Al ₂ O ₃ -I	4.7 18.7	227	9.0	214	0.94

^a Determined by EDS.

^b Determined after pyridine desorption at 100 °C.

was dried at 120 °C for 12 h; and then calcined at 500 °C for 6 h in order to assure the transformation of the Al₂O₃ to the γ phase. The W₂O₃/Al₂O₃-SG catalyst was prepared by adding the gelling aluminum alkoxide to a solution containing monohydrate ammonium tungstate to obtain 20 wt% of W₂O₃ in the final solid. For the preparation of the NiO–W₂O₃/Al₂O₃-SG catalyst, the same protocol described above was followed simultaneously adding nickel nitrate hexahydrate and monohydrate ammonium tungstate solutions to the gelling aluminum alkoxide in order to obtain 5 and 20 wt% of NiO and W₂O₃, respectively. The real composition was determined by EDS with an electron microscope JEOL 6490LV and the results are reported in Table 1.

The NiO–W₂O₃/Al₂O₃-I catalyst was prepared by incipient wetness impregnation of the sol–gel alumina support thermally treated at 500 °C with the solutions containing the monohydrate ammonium tungstate and nickel nitrate hexahydrate in the adequate amount to obtain the same content as in the NiO–W₂O₃/Al₂O₃-SG catalyst (5 and 20 wt% of NiO and W₂O₃, respectively). Before the characterization and catalytic tests, all the catalysts were dried and calcined at 500 °C for 4 h.

2.2. Characterization

The BET specific surface area of the samples was measured with a Quantachrome M3 Sorptometer. The X-ray diffraction (XRD) patterns were obtained by using Cu Kα radiation in a Siemens D-500 equipment. The number of acid sites was studied by following the pyridine adsorption with a FTIR Nicolet 710 spectrometer equipped with a cell of interchangeable windows, which allows thermal treatments. The sample was pressed into thin self-supported wafers and placed into the cell. Then, it was calcined at 400 °C in air for 4 h and evacuated (1×10^{-6} Torr) *in situ*. After cooling down to room temperature, pyridine was adsorbed and then fluxed with helium to eliminate the excess of pyridine. The spectra of the adsorbed pyridine were recorded at different desorption temperatures and the number of acid sites were estimated.

2.3. Catalytic activity

The catalytic activity was evaluated in the isobutene oligomerization by using a fixed bed reactor (5 mL). The evaluation procedure was carried out as follows: 0.1 g of catalyst was placed in the reactor; then, the temperature was increased until reaching the reaction temperature in air flow; once the desired temperature was reached, the air flow was stopped and then a mixture of isobutane/isobutene (40:60% (w/w)) was fed into the reactor at a GHSV value = 9.0 h⁻¹. The analysis of the products was done with a FID gas chromatographer (Varian Mod. CX3400) equipped with a PONA column of 50 m.

3. Results and discussion

The specific surface areas and the mean pore size diameter for the different synthesized solids were calculated by using the BET method from the corresponding nitrogen adsorption isotherms.

The pore size distribution was calculated by the BJH method plotted from the desorption branch to obtain a better accuracy in the calculation. The BET specific surface areas for the solids are reported in Table 1. In comparison with the reference alumina support (344 m²/g), the textural properties of the W₂O₃/Al₂O₃-SG catalyst are very similar, showing that the addition of the tungstate precursor to the alumina gelling medium does not alter the gelling process of the aluminum alkoxide. On the other hand, an important diminution of the BET specific surface area was obtained in the NiO–W₂O₃/Al₂O₃ catalysts; these values were of 227 and 121 m²/g for the impregnated and sol–gel preparations, respectively. The reduction of the specific surface area after the addition of the nickel and tungstate precursors by impregnation of the alumina support is a consequence of the deposition of the oxides on the surface of the catalyst. As for the sol–gel preparation, the effect on the specific surface area is more important; in such a case, the alumina gelling occurs in the presence of the solution containing both metal precursors and hence, the hydrolysis and condensation reactions of the aluminum alkoxide are perturbed, yielding a solid with lower specific surface area and smaller mean pore diameter size (Table 1).

The XRD spectra of the support and catalysts calcined at 500 °C were recorded; the corresponding values are shown in Fig. 1. It can be seen in all the samples the formation of γ-alumina, as well as the presence of W₂O₃ in the W₂O₃/Al₂O₃-SG sample. On the other hand, the spectra of the NiO–W₂O₃/Al₂O₃ catalysts do not show the peaks related to the presence of either NiO or W₂O₃. It must be noticed that the NiO and W₂O₃ content in both catalysts was of 5 and 20 wt%, respectively. Then, some small peaks in the XRD patterns due to the presence of these oxides should be observed. The fact that the peaks related to the metal oxides in the NiO–W₂O₃/Al₂O₃ catalysts prepared either by impregnation or by the sol–gel method are not observed, suggests that when both oxides are mixed, the nickel oxide induces effects on the formation of the W₂O₃ conglomerates. The nickel oxide could affect the growth of the tungsten oxide forming nanometric W₂O₃ clusters, which are not detectable by the XRD technique.

The olefin oligomerization reaction is carried out on solid acid catalysts [6,7,18–20]; the activity and specially, the selectivity of

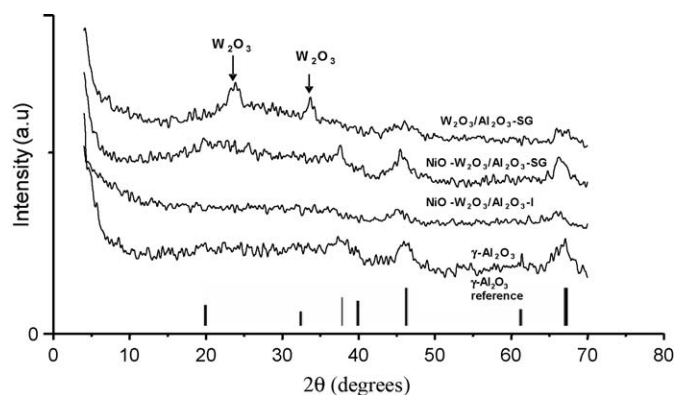


Fig. 1. XRD patterns for the NiO–W₂O₃/Al₂O₃ catalysts.

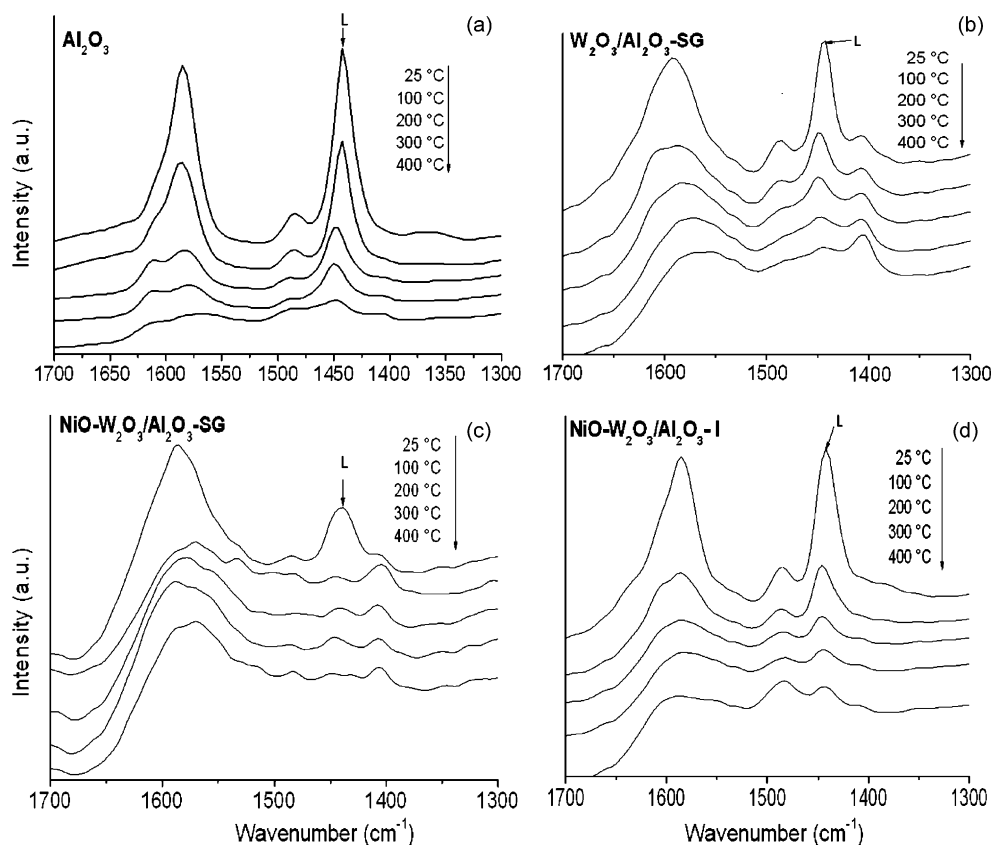


Fig. 2. FTIR pyridine absorption as a function of temperature for the NiO–W₂O₃/Al₂O₃ catalysts.

the reaction, strongly depend on the acid strength, distribution and type of acidity of the catalysts. In this way, the number of the acid sites of both the alumina support and the synthesized catalysts was determined by FTIR pyridine adsorption thermally desorbed at different temperatures; the corresponding spectra are shown in Fig. 2. The amount of pyridine desorbed as a function of temperature has been considered as an indirect method to determine the strength of the acid sites [25]. In a number of reported studies, the absorbance bands at 1590 and 1490 cm⁻¹ have been assigned to the simultaneous adsorption of the pyridine ion on Lewis and Brönsted acid sites, meanwhile the absorption band around 1450 cm⁻¹ has been assigned to the pyridine ion adsorbed only on Lewis acid sites; the adsorption on Brönsted acid sites was placed at around 1550 cm⁻¹ [7]. For the bare alumina support, the absorption band at around 1450 cm⁻¹ shows the presence of Lewis acidity. The absence of the absorption band at 1550 cm⁻¹ indicates that for this sample Brönsted acidity was not developed (Fig. 2a). Similar spectra were obtained for both the W₂O₃/Al₂O₃-SG and NiO–W₂O₃/Al₂O₃-SG catalysts, but in them, the band at 1450 cm⁻¹ is accompanied by a shoulder at around 1410 cm⁻¹, Figs. 2b and c, respectively. Until now, the identification of this band has not been possible; however, it is evident that its presence is the result of the sol–gel preparation method. For the NiO–W₂O₃/Al₂O₃-I catalyst, the FTIR pyridine adsorption spectra are shown in Fig. 2d, where the presence of Lewis acid sites can be clearly seen. The quantitative analysis for the 1450 cm⁻¹ band was done by integrating the absorption bands, after vacuum desorption of the adsorbed pyridine at different temperatures, following the method described in detail by Emeis [25]. The number of sites was calculated from 100 to 400 °C desorption spectra for the various catalysts and reported in Fig. 3. For a comparative study between the samples, the amount of pyridine adsorbed at 100 °C is shown in

Table 1, since at this temperature, it is considered that the physisorbed pyridine has been totally eliminated [25]. The results show that the number of the adsorbed pyridine molecules was 109, 170, 223 and 214 μmol/g for the Al₂O₃, W₂O₃/Al₂O₃-SG, NiO–W₂O₃/Al₂O₃-SG and NiO–W₂O₃/Al₂O₃-I samples, respectively. A remarkable effect that occurs when nickel and tungsten oxides coexist is that the number of Lewis acid sites is notably increased. Thus, the NiO could be formed by its own Lewis acid sites, which can also promote the W₂O₃ dispersion; and as a consequence, the number of total acid sites is increased.

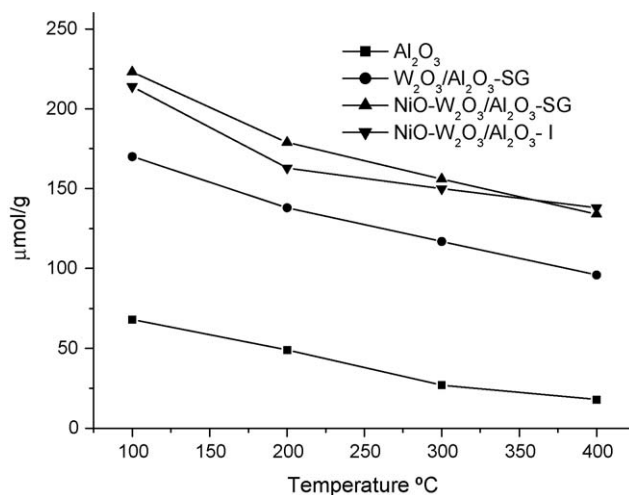


Fig. 3. Concentration of acid sites as a function of temperature for the NiO–W₂O₃/Al₂O₃ catalysts.

The activity in the isobutene dimerization was evaluated for the bare alumina support; and it shows a nil activity in the studied range of temperature (50–150 °C). For the W_2O_3/Al_2O_3 -SG catalyst, an extremely low conversion was obtained in the 50–150 °C temperature range. The latter could probably be due to the fact that they have a low number of Lewis acid sites in comparison with those of the $NiO-W_2O_3/Al_2O_3$ catalysts in which a synergetic effect produced by the formation of the $NiO-W_2O_3$ phase cannot be discarded.

The catalytic activity was determined for all the samples at 50, 100 and 150 °C and under the same conditions of GHSV and catalyst mass. In Fig. 4, the conversion evolution at 100 °C is illustrated as a function of time for the various catalysts. A very low activity can be seen for the W_2O_3/Al_2O_3 -SG catalyst, as it was mentioned before. On the other hand, for the W_2O_3/Al_2O_3 -SG catalyst, the initial conversion was of 27%; whereas for the impregnated preparation, it was of 12%. However, after 4.5 h on stream, the activity of the sol-gel preparation fell around 12%, meanwhile for the impregnated catalysts, the conversion oscillates around 8%. These results show that the sol-gel preparation is more active than the impregnated one, but it presents a highest deactivation. It is important to mention that the number and strength (Fig. 3) of the acid sites in both samples are of the same order (Table 1) and hence, the high initial conversion and deactivation shown by the sol-gel sample could be due to other factors rather than those related to the total acidity of the catalyst.

In Figs. 5 and 6, the selectivity behavior towards the $C_8^=$ olefin fraction as a function of time is shown. For the $NiO-W_2O_3/Al_2O_3$ -SG catalyst (Fig. 5), it can be seen that the selectivity towards the $C_8^=$ fraction noticeably diminishes with the time on stream, while with the impregnated catalyst, selectivity values as high as 100%, practically remains constant after 4.5 h on stream at the reaction temperatures of 50 and 100 °C. (Fig. 6). In Table 2, the conversion and selectivity values calculated after 4.5 h on stream for the various reaction temperatures are reported. For both the $NiO-W_2O_3/Al_2O_3$ catalysts, the conversion increases with temperature; however, the selectivity towards the $C_8^=$ olefin fraction shown by the sol-gel preparation increases from 42 to 66% in the 50–150 °C range, while for the impregnated catalyst, the selectivity diminishes from 100 to 81% in the same range of temperatures. This opposite effect as a function of temperature has also been observed on sulfated titania [8]; and it was explained by the presence of a mixture of gaseous and liquid olefins, whose ratio varies depending on the selectivity of the reaction and on the

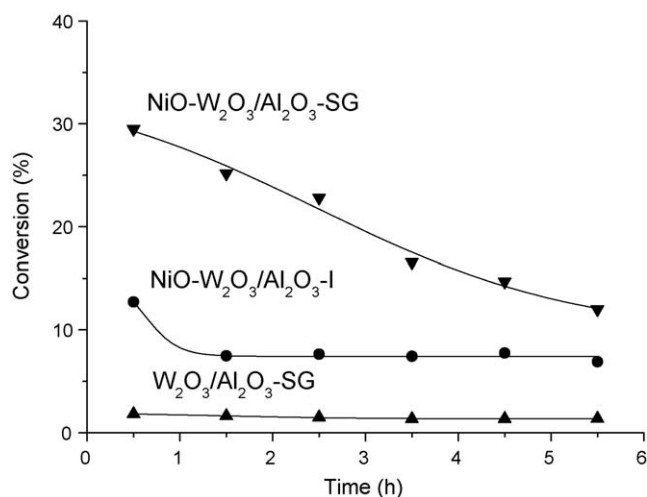


Fig. 4. Isobutene conversion at 100 °C as a function of time for the $NiO-W_2O_3/Al_2O_3$ catalysts.

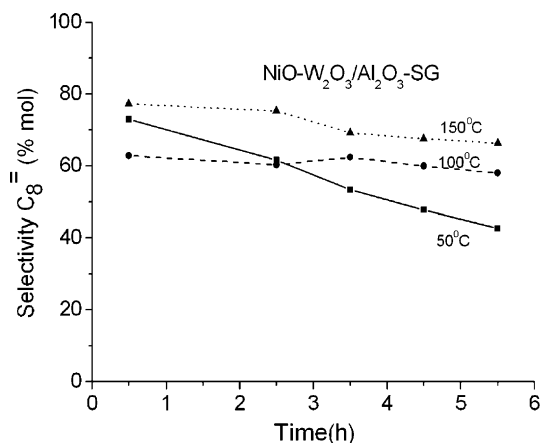


Fig. 5. Selectivity evolution towards the $C_8^=$ olefin fraction as a function of time for the $NiO-W_2O_3/Al_2O_3$ -SG catalyst.

temperature of the reactor [8]. For the catalyst with high initial selectivity to the $C_8^=$ fraction (impregnated), it diminishes at higher temperatures, where the $C_8^=$ olefin reaction with the isobutene of the gas phase is favorable. For the catalyst with low initial selectivity to $C_8^=$ (sol-gel), an important formation of $C_{12}^=$ and $C_{16}^=$ fractions is present in the reaction medium; however, at high temperatures, the splitting of the reaction occurs, i.e. decomposition of $C_{12}^=$ olefins forming $C_8^=$ and $C_4^=$ fractions. The effect of temperature on isobutene conversion as well as on oligomer distribution has also been studied by Alcántara et al. [26] over a range of 50–110 °C, using Amberlite-15 as acid catalyst. The authors report that at normal pressure and up to 100 °C the oligomers are in the liquid state, this favors the solubility of isobutene in the mixed phase of reaction mixture and the trimerization is accelerated. Above the boiling temperature of diisobutylene (approximately 110 °C), this effect is reversed and the formation of higher oligomers decreases, since oligomer splitting becomes an important side reaction above 100–110 °C. As a result, the selectivity towards the $C_8^=$ olefin fraction increases at higher reaction temperatures.

In Fig. 7, the selectivity of the W_2O_3/Al_2O_3 catalyst is shown to illustrate that on this catalyst with extremely low conversion (1–2.1%) a remarkable low selectivity to the $C_8^=$ fraction was obtained. These results demonstrate that the high selectivity obtained with the $NiO-W_2O_3/Al_2O_3$ -I catalyst is not a feature due to deactivation effects or the conversion level. The isobutene oligomerization

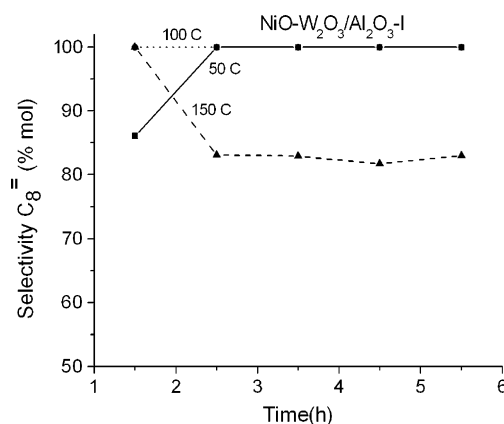
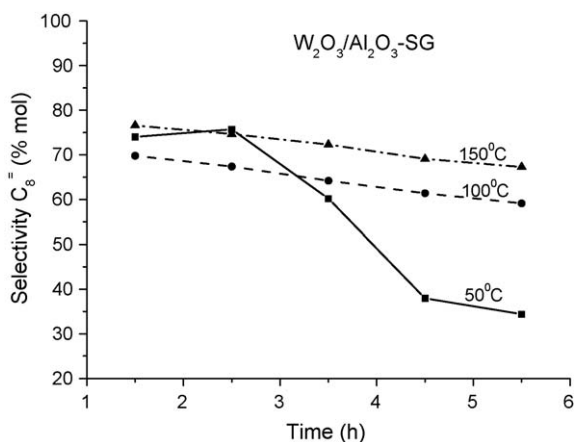


Fig. 6. Selectivity evolution towards the $C_8^=$ olefin fraction as a function of time for the $NiO-W_2O_3/Al_2O_3$ -I catalysts.

Table 2Total conversion of isobutene and selectivity to $C_8^=$ – $C_{16}^=$ olefins fractions at different temperatures.

Catalysts	Temperature (°C)	Selectivity			Yield to $C_8^=$ (% mol)	C^a (%)
		$C_8^=$ (% mol)	$C_{12}^=$ (% mol)	$C_{16}^=$ (% mol)		
W_2O_3/Al_2O_3 -SG	50	35	65	–	0.3	1.0
	100	64	36	–	0.8	1.3
	150	74	26	–	1.5	2.1
$NiO-W_2O_3/Al_2O_3$ -SG	50	42	57	1	3.1	7.4
	100	58	40	2	5.0	8.7
	150	66	33	1	9.6	14.6
$NiO-W_2O_3/Al_2O_3$ -I	50	100	–	–	6.2	6.2
	100	100	–	–	8.8	8.8
	150	82	18	–	12.1	14.8

^a $C_4^=$ conversion.**Fig. 7.** Selectivity evolution towards the $C_8^=$ olefin fraction as a function of time for the $NiO-W_2O_3/Al_2O_3$ -I catalysts.

reaction can be considered as a series of consecutive reactions, in which the formation of dimers, trimers or high molecular weight oligomers depends on the acid site strength as well as on their density on the surface of the catalyst. For the $NiO-W_2O_3/Al_2O_3$ catalysts prepared either by the sol-gel or impregnation method, the strength and the number of acid sites is quite similar. However, when the density of the acid sites was calculated per m^2 for the $NiO-W_2O_3/Al_2O_3$ -SG catalyst, it can be noticed that these acid sites doubled those obtained for the $NiO-W_2O_3/Al_2O_3$ -I catalyst (1.84 and $0.94 \mu mol/m^2$, respectively), Table 1. We can assume that the high selectivity towards the $C_8^=$ fraction obtained with the impregnated catalyst is due to the improved distribution of the active acid sites on the surface of the catalyst.

4. Conclusions

The results obtained with the $NiO-W_2O_3/Al_2O_3$ catalysts are promising for the industrial application in the production of ecological gasoline by means of the isobutene oligomerization, with an unexpected selectivity towards the $C_8^=$ olefinic fraction of 100%. As far as we know, it is the first time that the isobutene

dimerization has been obtained by using a solid acid catalyst in a gas phase reactor, under mild reaction conditions with so high a selectivity.

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