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Effect of nickel incorporation on the acidity and stability of HZSM-5 zeolite in the MTO process

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Abstract

A study has been carried on the effect of Ni incorporation on the acidity (acid strength distribution and total acidity), on the hydrothermal stability of a HZSM-5 zeolite and on the kinetic performance of this catalyst in the MTO process at high temperature (up to 500 °C, in order to increase selectivity to olefins) and when there is a high water content in the feed (in order to minimise deactivation by coke). The incorporation of Ni in the HZSM-5 zeolite implies a decrease in the total acidity and in the acid strength of the zeolite and, consequently, the activity of the catalyst decreases. Nevertheless, the catalysts with Ni are hydrothermally more stable than the parent zeolite catalyst. A Ni content around 1 wt% is the optimum, as it allows for uninterrupted operation in reaction–regeneration cycles, with water contents higher than 50 wt% in the medium, without irreversible deactivation, whereas a higher Ni content produces an unnecessary loss of initial activity.

Keywords: NiHZSM-5; MTO process; Acidity; Deactivation; Hydrothermal stability

1. Introduction

The methanol to olefins (MTO) process arose as a supplementary route to the initial objective of obtaining synthetic gasoline by means of the methanol to gasoline (MTG) process. Consequently, the catalyst chosen by Mobil for the MTO process was the HZSM-5 zeolite. Subsequently, it has been proven that selectivity to olefins increases when the zeolite is impregnated with metals [1,2], with an increase in temperature, as well as when water is fed with methanol [3–5]. Nevertheless, the role of water on the deactivation of the catalyst based on HZSM-5 zeolite in the transformation of methanol is a dual one, depending on the conditions under which the reaction is carried out. On the one hand, it has a beneficial effect because it attenuates the deactivation by coke deposition [6,7]. On the other hand, under extreme conditions (such as the high temperatures required for the MTO process) the presence of water has an unfavourable effect on deactivation because it dealuminates the zeolite [8,9].

Thus, although the HZSM-5 zeolite shows a moderate deactivation by coke in the MTO process, it suffers from irreversible deactivation (by dealuminisation) under the operating conditions required for a high yield of olefins $C_{2=}$–$C_{4=}$ (above 400 °C) and for minimizing coke deposition (≈50 wt% water in the feed). Due to this circumstance, the catalyst used in the commercial MTO process is SAPO-34 [10], which shows higher selectivity to light olefins than the several modifications carried out in the HZSM-5 (due to its high shape selectivity, with micropores of 3.8 Å, compared to those of around 5.5 Å in the HZSM-5) and it also shows higher hydrothermal stability. SAPO-34 undergoes very rapid deactivation by coke deposition [11–13], although activity is completely recovered subsequent to combustion of coke with air [14,15]. Consequently, the MTO process is based on two units (reactor and regenerator), which are interconnected fluidised beds with catalyst circulation from one to the other.

In this paper, the incorporation of Ni in the HZSM-5 zeolite is studied in order to modify its acid structure and to make it hydrothermally more stable, so that the catalyst may be used in a reaction–regeneration strategy similar to that presently used with SAPO-34. This stability must imply a

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minimum decrease in the activity of the catalyst. Results have been obtained by following reaction–regeneration cycles and the optimum conditions of the catalyst doped with Ni have been compared with those corresponding to the parent catalyst and to SAPO-34 catalyst.

2. Experimental

Different amounts of Ni have been incorporated on a commercial HZSM-5 (Si/Al = 30) by impregnation, which has been carried out in a rotary evaporator BÜCHI R-114 at 80 °C under vacuum, using solutions of Ni of variable concentration [16]. The final catalysts have been prepared by agglomerating the active phases (25 wt%) with a binder (bentonite, 30 wt%) and an inert solid (alumina, 45 wt%), in order to confer upon the final catalyst sufficient thermal and mechanical resistance for its use in the reactor. Prior to use, the catalyst is calcined at 575 °C for 2 h. The catalyst obtained under these conditions does not undergo appreciable dealumination when regenerated by coke combustion with air at 550 °C [17].

Surface acidity (acidic strength distribution and total acidity) of the different active phases (parent and modified zeolite) has been characterised by means of differential adsorption calorimetry of ammonia at 150 °C, and by temperature programmed desorption of ammonia using a ramp of 5 $^{\circ}C\ min^{-1}$ from 150 to 550 °C. Both measurements have been carried out in a Thermobalance SDT 2960 (TA Instruments) connected in series to a Mass Spectrometer (Balzers Instruments), for the monitoring of desorbed NH_3.

The kinetic behaviour of the final catalysts has been analysed in automated reaction equipment provided with an isothermal fixed bed reactor connected on-line to a gas chromatograph (Hewlett-Packard 6890) for the analysis of the reaction products (Fig. 1). The reactor is of 316 stainless steel with 9 mm internal diameter and 10 cm of effective length. At the reactor outlet, the reaction products pass through a 10-port valve, which allows for sending a sample to the gas chromatograph. The operating variables are controlled by means of Adkir process control software, which has been specifically designed for this process. The gas chromatograph is provided with detectors based on thermal conductivity (TCD) and flame ionisation (FID).

Hydrothermal stability has been analysed by means of reaction–regeneration cycles, under the following operating conditions: *Reaction stage*: temperature: 400, 450, and 500 °C; space time up to 0.159 $g_{catalyst}\ h/g_{methanol}$; water/methanol mass ratio in the feed 1; time on stream 3 h. *Regeneration step*: Coke combustion with air at 550 °C for 2 h, in order to completely eliminate coke without exceeding the calcination temperature of the catalyst [18], and consequently, to avoid deterioration of the acidic sites in the regeneration.

3. Results and discussion

3.1. Acidity characterisation

The results of acidity characterisation for the active phases of parent HZSM-5 zeolite and modified with different amounts of Ni are plotted in Fig. 2. The upper graph shows the acidic strength distributions, calculated as the ratio between the signals of heat flow and mass variation registered during the differential adsorption of ammonia at

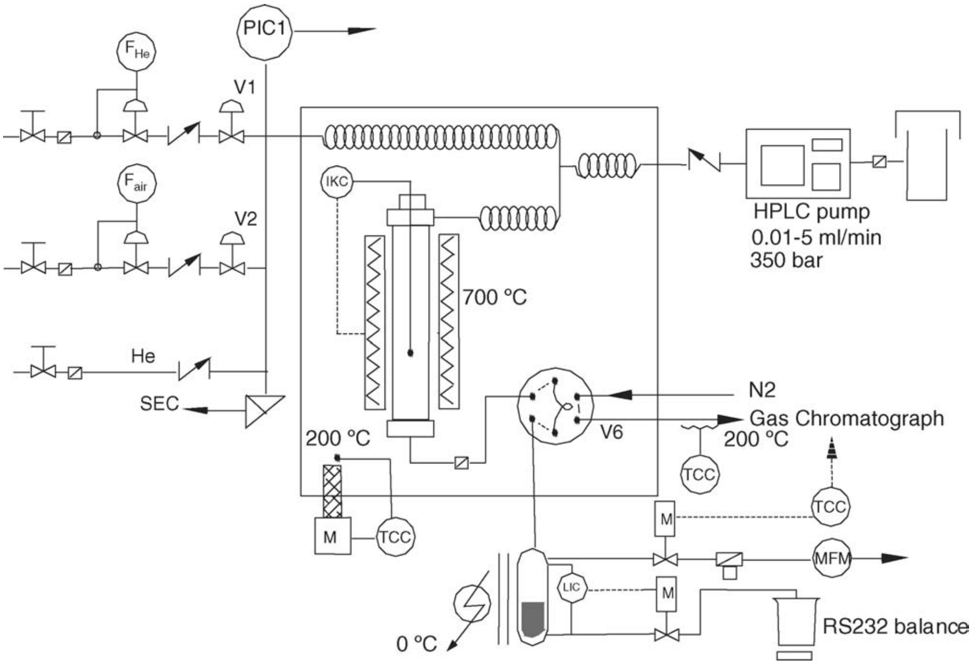

Fig. 1. Diagram of the reaction equipment.

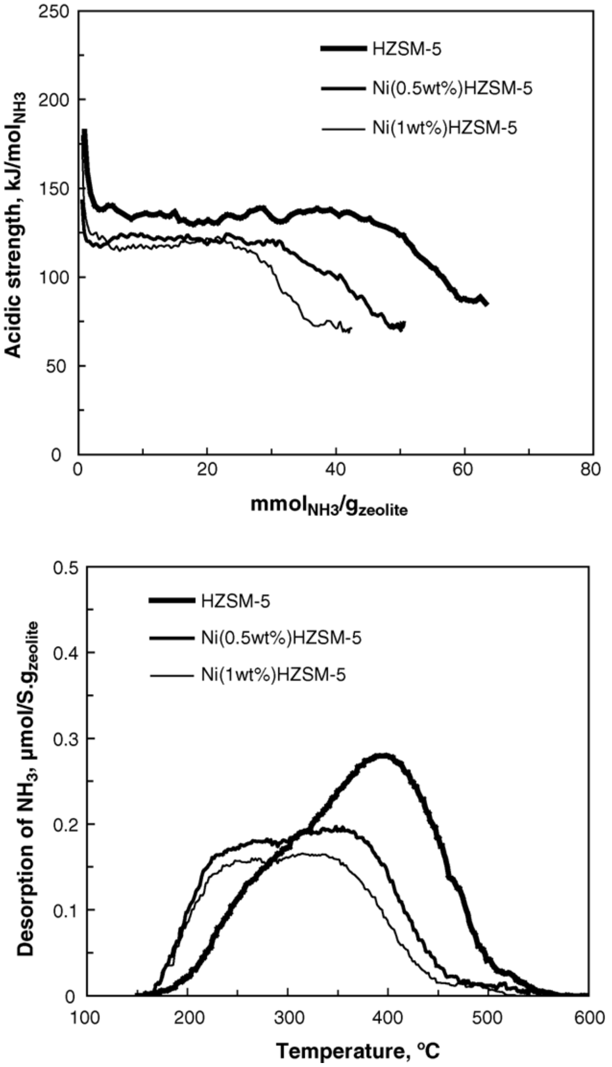

Fig. 2. Acidic strength distribution (upper) and TPD of NH_3 (lower) for the parent HZSM-5 zeolite and with different amounts of Ni.

150 °C, whereas the lower graph shows the results of TPD of NH_3.

It may be observed in this figure that the total amount of acidic sites decreases as the amount of Ni increases, and a slight decrease in the acidic strength is also observed. Thus, in the upper graph in Fig. 1, it is observed that the parent HZSM-5 zeolite has a total acidity of 0.61 (mmol of NH_3) (g of zeolite)$^{-1}$, with a majority of sites with adsorption heat of ≈140 kJ (mol of NH_3)$^{-1}$, whereas total acidity and adsorption heat of the stronger sites for Ni (1 wt%)HZSM-5 zeolite are, 0.41 (mmol of NH_3) (g of zeolite)$^{-1}$and 125 kJ (mol of NH_3)$^{-1}$, respectively.

Similar conclusions are drawn from the results of the temperature programmed desorption of ammonia (lower graph in Fig. 1). The results for parent zeolite show two peaks: the one corresponding to low strength, at 263 °C, which is weakly defined, and that corresponding to high strength, at 396 °C, which is very pronounced. It is observed that the temperature corresponding to the desorption peak at high temperature (strong sites) displaces towards lower temperatures as Ni content increase; thus, it diminishes to 340 °C for Ni (1 wt%) HZSM-5 zeolite. An increase in the proportion of weak sites (desorption peak at low temperature) is also observed with Ni incorporation, although the relative proportion of weak to strong sites is almost constant with the amount of Ni.

3.2. Kinetic behaviour in the transformation of methanol

The effect of operating temperature on the catalytic activity and selectivity to olefins for the different catalysts has been analysed by means of dynamic experiments following a temperature ramp of 7 °C min^{-1} from 250 to 450 °C, and subsequently maintaining this temperature constant for 2 h. Fig. 3 shows the evolution with time of the total conversion of oxygenates (X_T), and of the yield of light olefins (X_O) for the parent catalyst and modified zeolites. It is observed that as nickel content is increased, catalyst activity decreases, and consequently, a higher reaction temperature is required for initiating oxygenate transformation into hydrocarbons. Furthermore, total conversion of oxygenates is not reached in the whole range of temperatures studied, from 250 to 450 °C, and the maximum value of conversion is lower as the content of Ni is higher.

Selectivity to olefins (X_O/X_T) is higher for the catalysts with nickel than for the parent zeolite. Thus, at 425 °C, selectivity to olefins for the catalyst based on Ni (1 wt%) HZSM5 zeolite is 0.60, which is a significantly higher value than that corresponding to the parent zeolite (0.47), although, due to its lower activity, the maximum yield of olefins for Ni (1 wt%) HZSM-5 (0.40 at 435 °C) is considerably lower than that corresponding to the

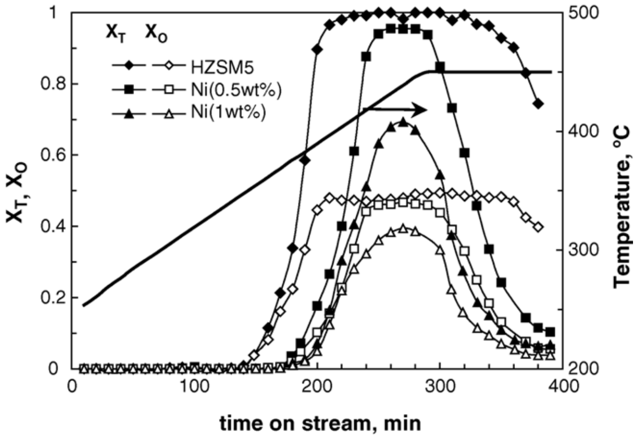

Fig. 3. Evolution with time on stream of total conversion (X_T) and yield of $C_{2=}$–$C_{4=}$ olefins (X_O) for catalysts made up of the parent HZSM-5 zeolite and modified with Ni. Reaction conditions: temperature ramp, 0.7 °C min^{-1}; 50 wt% of water in the feed; space time 0.132 $g_{catalyst}$ h/g_{MeOH}.

parent zeolite catalyst (mean value of 0.45 in the 400–450 °C range) at the experimental conditions of Fig. 3. Nevertheless, it has been proven that at the same temperature and for a similar total conversion, the selectivity to olefins reached with the catalysts with Ni is similar to that corresponding to the parent zeolite, and consequently, the maximum yield of olefins is also similar.

In the period shown in Fig. 3, for which temperature is maintained constant at 450 °C, it is observed that deactivation of catalysts with Ni is more rapid than that of the parent zeolite. Nevertheless, it must be taken into account that this result is partly due to the different total conversion, and consequently, to the different composition of the reaction medium. It must be taken into account that the main cause of coke deposition is oxygenates (methanol + dimethyl ether) that are irreversibly adsorbed on the catalyst [6,7,9]. The difference in deactivation attenuates when space time is increased for the catalysts with Ni.

The effect of Ni incorporation on hydrothermal stability is shown in Fig. 4. This figure shows results of total conversion at the reactor outlet in successive reaction steps at 450 and 500 °C (with regeneration between cycles). Given the lower activity of the catalysts with Ni, these catalysts require three-times higher space time than the parent catalyst for attaining total conversion of oxygenates. Nevertheless, it is observed that for the parent zeolite catalyst, the conversion progressively decreases from one cycle to another. This irreversible loss of activity is a consequence of the dealumination of the zeolite and entails acidity deterioration. Nevertheless, the catalyst with 1 wt% Ni completely recovers its initial activity in the successive cycles studied. This is the optimum amount of Ni, as for lower contents irreversible deactivation persists and higher contents lead to decrease in activity.

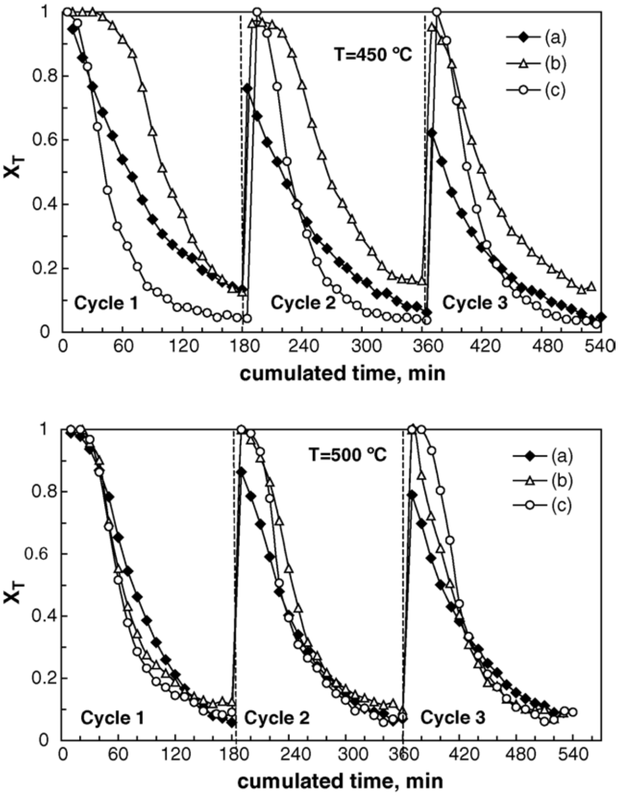

Fig. 4. Evolution with time on stream of total conversion throughout successive reaction–regeneration cycles. (a) Parent zeolite, 0.053 $g_{catalyst}\,h/g_{MeOH}$; (b) Ni (0.5 wt%) HZSM-5, 0.159 $g_{catalyst}\,h/g_{MeOH}$; (c) Ni (1wt%) HZSM-5, 0.159 $g_{catalyst}\,h/g_{MeOH}$.

In Fig. 5, the results of evolution with time on stream of the yields of $C_{2=}$–$C_{4=}$ olefins for catalysts prepared based on the parent HZSM-5 zeolite, Ni (1 wt%) HZSM-5 zeolite and SAPO-34, are compared. These results are evidence that the catalyst based on Ni (1 wt%) HZSM-5 zeolite is an interesting alternative to SAPO-34 because of its significantly lower deactivation by coke. It is noteworthy than the results plotted for SAPO-34 catalyst correspond to a higher space time. Furthermore, the reaction temperature used with the catalyst prepared with the parent HZSM-5 zeolite is 400 °C, which is the maximum allowable for avoiding irreversible deactivation. It is observed that the catalyst based on Ni (1 wt%) HZSM-5 zeolite gives a higher initial yield of olefins (56%) with respect to that of the parent zeolite (42%), although coke deposition is higher (as a consequence of the higher operating temperature). It should be noted that, although SAPO-34 has higher selectivity to olefins, its deactivation by coke is much faster and it has lower activity than the other catalysts.

In any case, operation in the MTO process is carried out in fluidised bed with catalyst circulation, and consequently, the three catalysts are suitable, but with different optimum flowrates (optimum mean residence times). Hydrothermal stability is an essential property that advises against using the parent HZSM-5 zeolite, because even at 400 °C it does not fully recover its activity when operation is carried out in successive reaction–regeneration cycles.

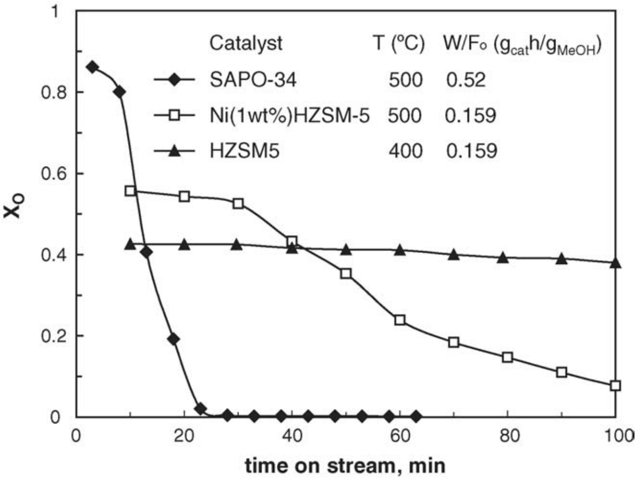

Fig. 5. Evolution with time on stream of the yield of olefins in the MTO process for the different catalysts.

4. Conclusions

The incorporation of Ni in the HZSM-5 zeolite implies a decrease in total acidity and in the acid strength of the zeolite. Consequently, the activity of the catalyst decreases and a higher space time is required for complete conversion of methanol to hydrocarbons.

Nevertheless, the catalysts with Ni are hydrothermally more stable than the parent zeolite catalyst, and activity is completely recovered in the operation under reaction–regeneration cycles. Consequently, the incorporation of Ni in the zeolite is a suitable solution for using it in processes that require very severe operating conditions (high temperature and water content), such as the MTO process. A Ni content around 1 wt% is the optimum, as it allows for uninterrupted operation in reaction–regeneration cycles, at 500 °C with water contents higher than 50 wt% in the medium, without irreversible deactivation. A higher Ni content produces an unnecessary loss of activity.

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