

Supporting Information

Intensifying propylene production by 1-butene transformation on a K modified HZSM-5 zeolite catalyst

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1. Catalyst, Reaction Equipment and Product Analysis

1K/HZ-280 catalyst was prepared based on a HZSM-5 zeolite of $\text{SiO}_2/\text{Al}_2\text{O}_3=280$ (Zeolyst International) that was calcined at 570 °C to obtain the acid form (denoted HZ-280). Impregnation of 1 wt % K was carried out by slowly adding a KOH solution onto the acid form of the HZ-280 zeolite, under vacuum (in a Rotavapor) at 70 °C. The modified zeolite was agglomerated with a binder (bentonite, Exaloid) (30 wt %) and an inert charge (alumina, Martinswek, calcined at 1000 °C) (45 wt %). The catalyst particles were obtained by wet extrusion. They were first dried at room temperature for 24 h and then sieved to a particle diameter of between 0.15 and 0.3 mm. The particles were dried in an oven at 110 °C for 24 h and then calcined at 570 °C for 2 h. The agglomeration of the active phase does not significantly reduce acidity, but provides the catalyst with a matrix having mesopores and macropores, which contributes to reducing deactivation by coke deposition¹ and to increasing the hydrothermal stability in the regeneration step by coke combustion.² The validity of the synthesis method has been proven by ensuring the reproducibility of catalyst properties.

Table S1 sets out the physical properties of the catalyst. The porous structure has been determined by N_2 adsorption–desorption (Micromeritics ASAP 2010) and Hg porosimetry (Micromeritics Autopore 9220). The micropore volume corresponds to the

crystals of the HZSM-5 zeolite, whereas the volume of meso- and macropores corresponds to the matrix of the catalyst (bentonite and alumina). It should be mentioned that the method of doping with K does not appear to provide any additional mesopores by partial destruction of the HZSM-5 zeolite crystalline structure. This destruction has not been observed by XRD either.

Table S1. Physical properties of the fresh catalyst (1K/HZ-280)

Property	Value
$d_p, \text{\AA}$	78
$S_{\text{BET}}, \text{m}^2 \text{g}^{-1}$	194
$S_m, \text{m}^2 \text{g}^{-1}$	85
$V_m, \text{cm}^3 \text{g}^{-1}$	0.037
$V_p [17 < d_p (\text{\AA}) < 3000], \text{cm}^3 \text{g}^{-1}$	0.18
Distribution of volume, vol %	
$d_p (\text{\AA}) < 20$	3.0
$20 < d_p (\text{\AA}) < 500$	46.5
$d_p (\text{\AA}) > 500$	50.5

The values of total acidity and acid strength of the zeolite modified with 1 wt % K (1K/HZ-280) are shown in Table S2 together with the results corresponding to the parent zeolite (HZ-280). These results have been determined by means of adsorption-desorption of tert-butylamine (*t*-BA), by combining the techniques of thermogravimetric analysis and differential scanning calorimetry (at 150 °C) followed by temperature programmed desorption (a ramp of 5 °C min⁻¹ to 550 °C), and using a Setaram TG–DSC calorimeter connected on-line with a Thermostar mass spectrometer from Balzers Instruments.³ The incorporation of 1 wt % K selectively eliminates strong acid sites, which is consistent with previous results in the literature,⁴⁻⁶ and gives way to a better redistribution of the acid site nature for selectively obtaining propylene.³

Table S2. Total acidity, average acid strength and desorption peaks obtained by *t*-BA-TPD for the parent and 1 wt % K modified zeolites.

Zeolite	Total acidity, mmol (g _{zeolite}) ⁻¹	Average acid strength, kJ mol ⁻¹	T of TPD peaks	
			1 st peak	2 nd peak
HZ-280	0.15	112	204	253
1K/HZ-280	0.13	75	245	-

It has been proven that the agglomeration with bentonite and alumina does not confer any substantial acidity to the final catalyst; thus, the total acidity per mass unit in the final catalyst is a quarter of the acidity corresponding to the zeolite due to its dilution with bentonite and alumina.

The coke content deposited on the catalyst was determined by temperature-programmed oxidation (TPO) in a SDT 2960 thermobalance (TA Instruments), by a well established procedure in the literature.^{3,7,8}

Experimental runs have been carried out using an equipment described in a previous work.³ The fixed-bed reactor, made of 316 stainless steel, has an internal diameter of 0.9 cm and a length of 10 cm. The bed consists of a mixture of catalyst and inert solid (carborundum with an average particle diameter of 0.105 mm to ensure bed isothermality and attain sufficient height under low space time conditions). The temperature is controlled by a digital TTM-125 series controller and measured by a thermocouple (type K) situated in the catalyst bed. Two additional temperature controllers are used: one for the furnace chamber and one for the transfer line between the reactor and the micro-gas chromatograph. The operating variables are controlled by custom built software (Process@ from PID Eng&Tech, Madrid, Spain).

The products have been analyzed every 4 min in a micro-gas chromatograph (Agilent MicroGC 3000A) provided with 4 analytical modules and the corresponding columns

(MS-5A, PPQ, Alumina, and OV-1). The compounds have been identified and quantified using calibration standards of known concentration. The balance of atoms (C, H) was closed in all runs above 99.5%.

References

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