

The role of silanol and OH groups of HY zeolite in cyclohexene conversion: an FT-IR operando study

Bruno M. Santos*^{1,3} José L. Zotin¹, Françoise Maugé², Laetitia Oliviero², Weitao Zhao² and Mônica A. P. da Silva³

¹Hydrorefining and Special Processes Division, R&D Center, PETROBRAS, Rio de Janeiro (Brazil)

²Normandie Univ, ENSICAEN, UNICAEN, CNRS, LCS, 14000 Caen (France)

³Universidade Federal do Rio de Janeiro, Escola de Química, Centro de Tecnologia, Bloco E, Ilha do Fundão, Rio de Janeiro (Brazil)

[*bruno_m@petrobras.com.br](mailto:bruno_m@petrobras.com.br)

S1. Coverage after cut of cyclohexene flow during test 1

At the end of test 1, cyclohexene flow was cut off, and the system was kept under 100 ml min⁻¹ of N₂ at 523 K for 0.6 h. The coverage (θ) of each group, measured before and 0.6 h after cyclohexene cut, as well as the concentration of coke and intermediate species, are shown in Table S1.1. Only silanol and OH groups in hexagonal prisms presented a decrease in their coverage. Besides, no decrease of coke was observed, while intermediate species presented a small reduction, but did not disappear.

Table S1.1. Coverage of silanol and OH groups, as well as coke and intermediate species concentration.

	Before cut of cyclohexene flow	0.6 h after cut
θ 3516 cm ⁻¹ (Hexagonal prisms OH)	0.80	0.75
θ 3541 cm ⁻¹ (Perturbed OH sodalite cages)	0.97	0.97
θ 3558 cm ⁻¹ (Non-perturbed OH sodalite cages)	0.98	1.00
θ 3606 cm ⁻¹ (Perturbed OH supercages)	0.86	0.88
θ 3625 cm ⁻¹ (Non-perturbed OH supercages)	0.75	0.74
θ 3739 cm ⁻¹ (SiOH groups)	0.81	0.75
Coke (area g ⁻¹)	1279	1274
Intermediate species (area g ⁻¹)	28	22

S2. Intermediate species with TOS

Evolution of intermediate species with time on stream (TOS) during test 1 was calculated by the area of band at 1496 cm^{-1} and shown in Figure S2.1. The quantification of such species during test 2 was not possible due to the overlapping between this band and the one related to pyridine adsorption at 1490 cm^{-1} .

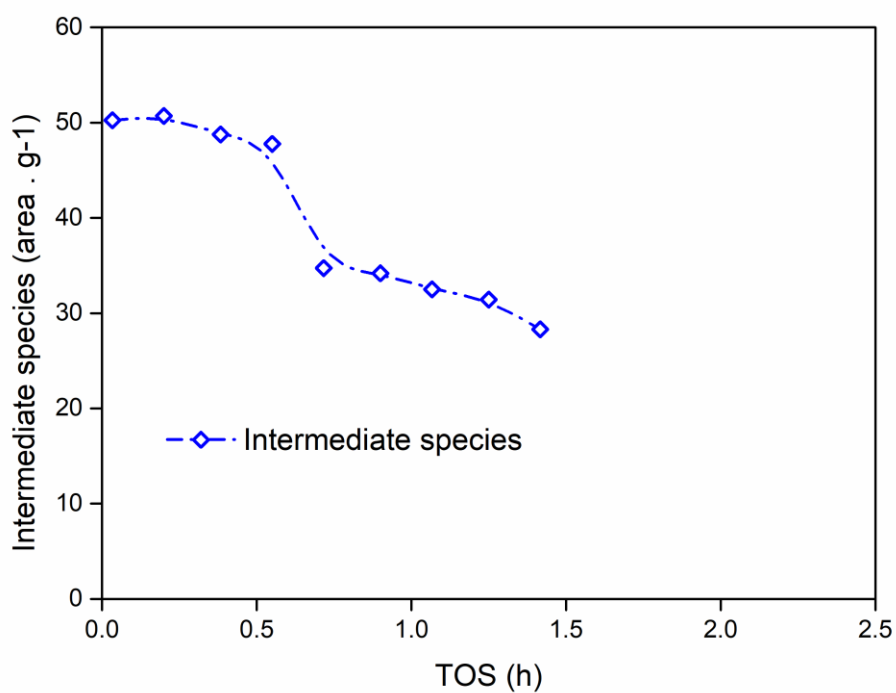


Figure S2.1. Evolution of intermediate species with TOS.

S3. Test with pure silica

Experimental

This test was performed with silica gel Si 60 (40-63 μm , Merck). Firstly, silica was activated at 623 K for 2.5 h (heating rate of 3 K min^{-1}) under a flow of 30 mL min^{-1} of N_2 . After that, the temperature was decreased to 523 K at a ramp of 3 K min^{-1} . Then, the reaction gas (1.3 % of cyclohexene and 98.7 % of N_2 , molar basis) was added to the cell. The temperature used in the test was 523 K, and the reaction gas flow was 100 mL min^{-1} . FTIR spectra of the catalyst surface were recorded on a Nicolet 6700 equipped by an MCT detector with 64 scans and 4 cm^{-1} resolution. At the same time, the composition of reactor effluent was determined by GC, utilizing a Bruker 450-GC equipment, equipped with a column BP1 50 m x 0.32 mm and a FID. Cyclohexene conversion (X) and product yield (Y) were calculated as described in Eqs. (1) and (2), respectively, in the main paper. Coverage of silanol groups (θ) was calculated by Equation (5) in the main paper, using the area of the band spectrum at 3739 cm^{-1} .

Results

The silica spectrum in the silanol region is shown in Figure S3.1. This material presented only a band at 3739 cm^{-1} , corresponding to silanol (SiOH) groups [1].

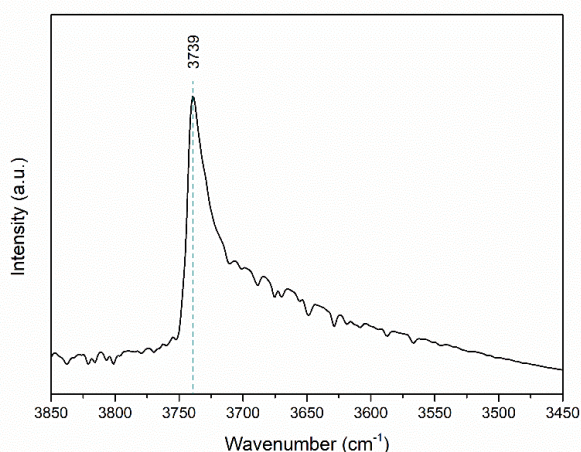


Figure S3.1. Spectrum of silica in the silanol region.

After the introduction of cyclohexene, no bands of coke and intermediate species were observed by IR spectra. Cyclohexene conversion and product yield were negligible (less than 0.1 %), as well as SiOH coverage (maximum of 0.04). Results are shown in Figure S3.2, and according to West *et al.* [2], silica is not inactive for isomerization reactions, but the addition of a small amount of Al provides substantial activity.

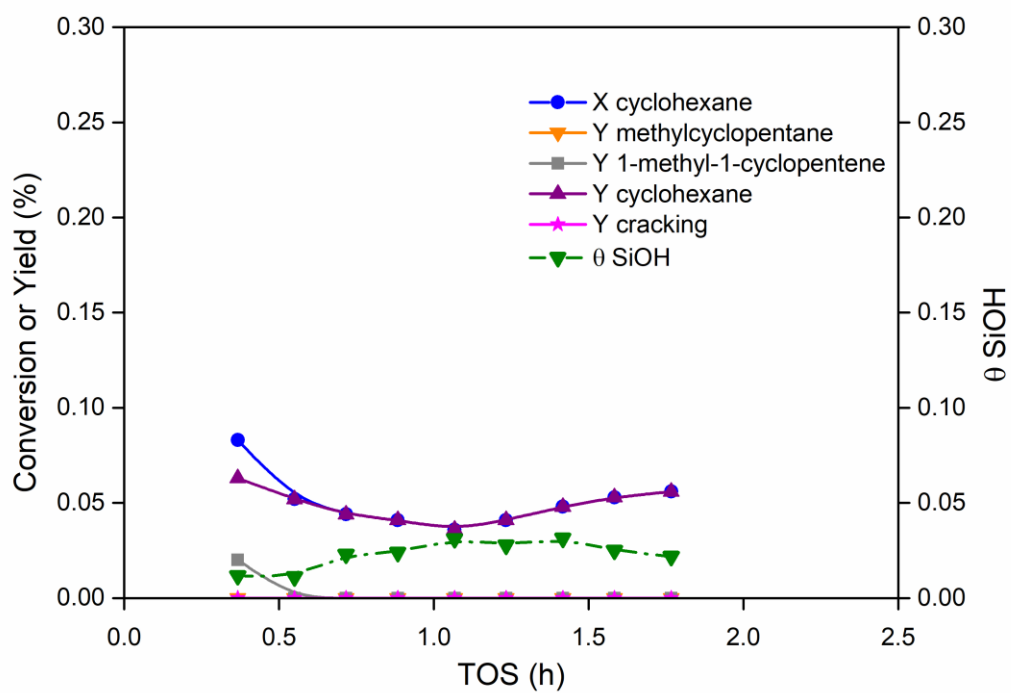


Figure S3.2. Cyclohexene conversion, product yield and silanol coverage results on silica.

References

1. Gabrienko AA, Danilova IG, Arzumanov SS, Pirutko L V, Freude D, Stepanov AG (2018) *J Phys Chem C* 122:25386–25395
2. West PB, Haller GL, Burwell RL (1973) *J Catal* 29:486–493