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Journal of Molecular Catalysis A: Chemical 108 (1996) L1–L3

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

Letter

Interaction of propane with H-ZSM-5 and Ga/H-ZSM-5 as studied by IR spectroscopy

P. Mériaudeau *, J.F. Dutel

Institut de Recherches sur la Catalyse – CNRS, 2 av. A. Einstein, 69626 Villeurbanne Cedex, France

Received 4 December 1995; accepted 12 December 1995

Abstract

The interaction of propane with H-ZSM-5 and Ga/H-ZSM-5 was studied through the exchange of C_3D_8 with the protons of the zeolite. The rate of exchange is faster for the Ga/H-ZSM-5 solid, indicating that the first step of propane activation is not the same for the two solids.

The aromatization of lower alkanes has received detailed attention recently [1,2]. Despite the large number of investigations, some steps of this reaction remain unclear, in particular the first step of the alkane activation [3]. Here, we report on preliminary experiments and results relative to the interaction of propane with H-ZSM-5 and Ga/H-ZSM-5 solids as studied by IR spectroscopy. For this purpose, we have used catalysts which were fully described previously [3] H-ZSM-5 ((Si/Al) = 15) and Ga/H-ZSM-5 (1 wt% Ga, incipient wetness impregnation with $Ga(NO_3)_3 \cdot 9H_2O$) were pressed into thin wafers (15 mg), mounted in an IR cell allowing thermal treatments. The samples were first treated in situ in flowing O_2, Temperature being increased from RT to 773 K (4 h at 773 K), then flushed with N_2 before heating in flowing H_2 (4 h at 773 K); they were finally outgassed for 2 h at 773 K ($P = 10^{-4}$ kPa) and cooled down to RT. Both IR cells have the same volume. Labelled C_3D_8 (99,5%, Isotech, France) was used.

The initial spectrum of the H-ZSM-5 catalyst treated and outgassed at 773 K is represented in Fig. 1a (Fig. 2a for Ga/H-ZSM-5 in the same experimental conditions: it appears that, on both the catalysts, terminal silanol groups (νOH = 3740 cm^{-1}) and bridging OH groups (3610 cm^{-1}) are visible.

Spectra depicted in Fig. 1b for H-ZSM-5 and in Fig. 2b for Ga/H-ZSM-5 have been obtained upon contacting the samples with 0.7 kPa of C_3D_8 at room temperature.

Both spectra (1b and 2b) showed that the Brønsted OH groups are interacting with the alkane (broadening of the OH vibrations and shift towards 3500 cm^{-1}; in contrast, terminal silanol vibrations are unchanged.

Indeed, the gas phase vibration of C_3D_8 are observed (νCD_3 = 2218 cm^{-1}) and surprisingly a weak vibration is appearing at 2587 cm^{-1} for

* Corresponding author.

SSDI 1381-1169(95)00298-7

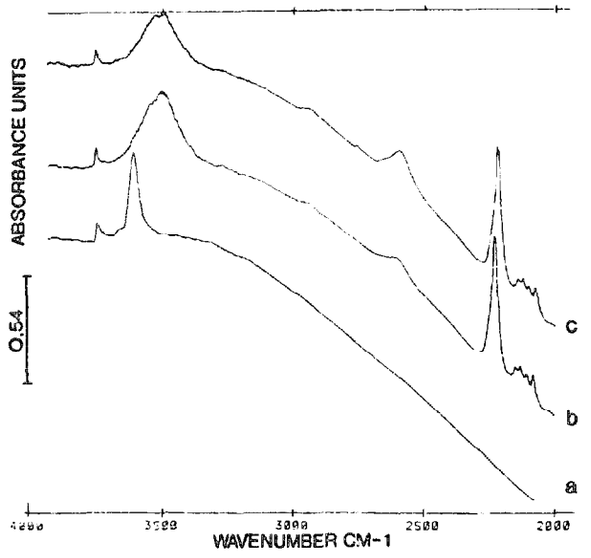

Fig. 1. IR spectra of H-ZSM-5 sample, (a) after treatment and outgassing at 773 K, (b) contacted with C_3D_8 at RT, (c) as b and heated for 30 min at 673 K.

both samples. If the catalysts are maintained at RT for 30 additional minutes, no change is observed.

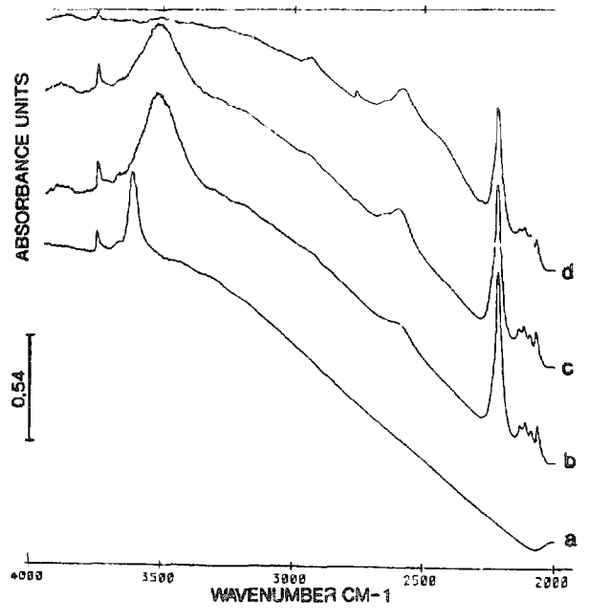

Fig. 2. IR spectra of Ga/H-ZSM-5 sample, (a) after treatment and outgassing at 773 K, (b) contacted with C_3D_8 at RT, (c) as in b and heated for 5 min at 673 K, (d) as in c and heated for 25 additional min at 673 K.

At this stage, the two catalysts were heated at 673 K, 5 min, for Ga/H-ZSM-5 (spectrum 2c) and for 30 min for H-ZSM-5, (spectrum 1c).

It is clear that after 5 min at 673 K, part of the OH groups of Ga/H-ZSM-5 have been exchanged with deuterium (decrease of the OH vibration at 3500 cm^{-1} and increase of the OD vibration at 2590 cm^{-1}; in addition it is observed that a new vibration (at 2960 cm^{-1}) is growing. Similar conclusions are deduced from the comparison of Fig. 1b with Fig. 1c.

If the Ga sample is heated at 673 K for an additional period of 25 min, (spectrum 2d) it is observed that the OH vibration at 3500 cm^{-1} has completely disappeared while the OD vibration (2587 cm^{-1}) has increased. Comparison of spectra 1c (H-ZSM-5 heated for 30 min at 673 K) with 2d (Ga/H-ZSM-5 heated for 30 min at 673 K) indicates that the rate of exchange of OH groups with deuterium from C_3D_8 is faster for the Ga sample. Comparison of Fig. 2b with Fig. 2d indicates a growth of the vibration at 2960 cm^{-1} and comparison of Fig. 2d with Fig. 1c indicates that this vibration is greater for Ga/H-ZSM-5 compared to H-ZSM-5. This vibration is attributed to the C–H vibration of CHD_2 [4] and results from the transformation of CD_3 group of propane into CHD_2 via exchange with the protons of the catalysts.

It is not known if the same exchange mechanism is operating on both catalysts. Various mechanisms were proposed for ^{13}C scrambling in propane over H-ZSM-5 and Ga/H-ZSM-5 [5,6]; the intermediates postulated for ^{13}C scrambling could also operate for H/D exchange.

In situ IR experiments are now planned in order to identify the effect of the reaction temperature and of propane pressure on the rate of H/D exchange (H belonging to OH groups, D to C_3D_8). These results will be of help to propose a mechanism for H/D exchange over the two catalysts and to understand the role of the added gallium.

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