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Revisiting Ga_2O_3/H-ZSM-5 propane aromatization catalysts

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Oxidative or reducing treatments at 873 K of Ga_2O_3/H-ZSM-5 (Si/Al = 13 or 60) cause a change in H^+ concentration as evidenced by IR spectroscopy of OH groups at 3610 cm^{-1}; this change is nicely correlated to the variation of *m*-xylene isomerisation rate.

Keywords: Ga_2O_3/H-ZSM-5; *m*-xylene isomerisation

1. Introduction

Short chain alkane aromatization reactions have been extensively studied and recently reviewed [1,2]. Guisnet et al. [3], in a recent issue of this journal, have used model reactions to evidence the neutralization of the acid sites of Ga/H-ZSM-5 catalysts caused by hydrogen pretreatment; the test reaction used, *m*-xylene isomerisation, is a reaction uniquely catalyzed by protons. In their paper, the authors concluded that the decrease in the activity for *m*-xylene isomerisation caused by hydrogen pretreatment is much smaller than the decrease in the number of protons expected from the model proposed by Kanazirev and Price [4] and illustrated by use of IR spectroscopy as shown by Mériaudeau and Naccache [5]. The published data [4,5] unambiguously indicate that the H^+ number decreased following H_2 treatment of Ga_2O_3/H-ZSM-5.

In addition, it is generally observed that the catalytic activity in *m*-xylene isomerisation is directly proportional to the number of acid sites. In order to contribute to the apparent discrepancy existing between the work of Guisnet et al. [3] and the data given in refs. [4,5], we have reinvestigated the neutralization of the acid sites of H-ZSM-5 with gallium using two H-ZSM-5 having different number of acid sites (Si/Al = 13 and Si/Al = 60). IR spectroscopy was utilized to evidence directly the change in proton concentration as a function of the thermal treatment and *m*-xylene isomerisation (which is catalyzed by protons) was used as an indirect measurement of the proton concentration.

2. Experimental

H-ZSM-5 samples with Si/Al = 13 and Si/Al = 60 were prepared according to ref. [6]; as described in ref. [5], Ga_2O_3 (5 wt% Ga) was deposited onto the supports using gallium nitrate (Aldrich) (incipient wetness technique [5]). Samples, after drying in air overnight at 373 K, were calcined in a flow of O_2 at 773 K (8 h).

2.1. IR STUDIES

The as-prepared samples were pressed into small wafers (= 10–12 mg) and introduced in a special quartz cell allowing thermal treatments in dynamic conditions. Spectra were registered with a Brucker IFS48 spectrometer on samples having been first oxidized overnight at 873 K in a flow of dry oxygen and on samples having been first oxidized and then reduced under a flow of *dry* H_2 for 12 h; before registration of the spectra, samples were out-gassed for 1 h ($p = 0.1$ Pa).

2.2. CATALYTIC TEST: *m*-XYLENE ISOMERISATION

The catalysts were treated as previously stated for IR studies. For the test reaction, the temperature was decreased in the range of 453–603 K (see results); *m*-xylene pressure was fixed to 0.23 kPa, the diluent gas, to have total pressure equal to 101 kPa, being *dry* helium. Catalyst weight was fixed to 10 or 20 mg and flow rates adjusted between 2 and 8 ℓ/h. In each case, it has been checked that the rate of *m*-xylene isomerisation was independent of the flow rate.

Reactant and products (*p*- and *o*-xylene) were analyzed on-line with a FID gas chromatograph equipped with a Bentone column.

3. Results and discussion

3.1. INFRARED

In fig. 1 are reported the spectra obtained on 5% Ga/H-ZSM-5 (Si/Al = 60) after the oxidative treatment and the reducing treatment. Fig. 2 shows the spectra obtained on 5% Ga/H-ZSM-5 (Si/Al = 13). From these figures, it is clearly observed that the IR band intensity at 3610 cm^{-1}, due to acidic OH groups, is strongly reduced after the reducing treatment for both samples indicating that upon Ga_2O_3 addition to H-ZSM-5 and reduction under hydrogen, the number of protons is considerably decreased. These results are in good agreement with those reported earlier for the most acidic zeolite [5] and indicate that the behaviour of the less acidic catalyst follows the same trend, suggesting that the model proposed by Price et al. [4] ($Ga_2O_3 + 2HZ + 2H_2 \rightarrow 2GaZ + 3H_2O$) is valid for H-ZSM-5 solids having Si/Al ranging from 13 to 60. From figs. 1 and 2, it is difficult to quantify

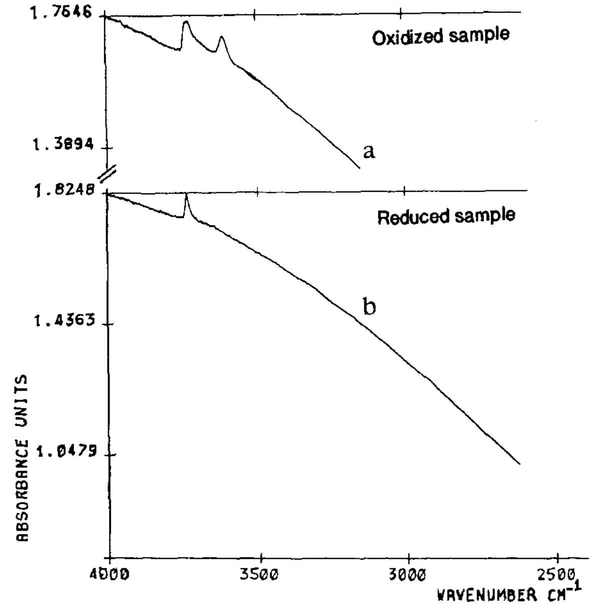

Fig. 1. Infrared spectrum of Ga_2O_3/H-ZSM-5 (Si/Al = 60); (a) after oxidation 873 K, (b) after reduction 873 K.

precisely the decrease in concentration of the acid groups. One can estimate that the number of protons is decreased by a factor of 20–30.

3.2. CATALYTIC RESULTS

In figs. 3 and 4 are depicted log $V_{p\text{-xylene}} = f(1/T)$ for the two catalysts treated under oxidative and reducing conditions. It is observed that the reaction rates obey an Arrhenius law at low temperature and deviated from the linear curve as the tem-

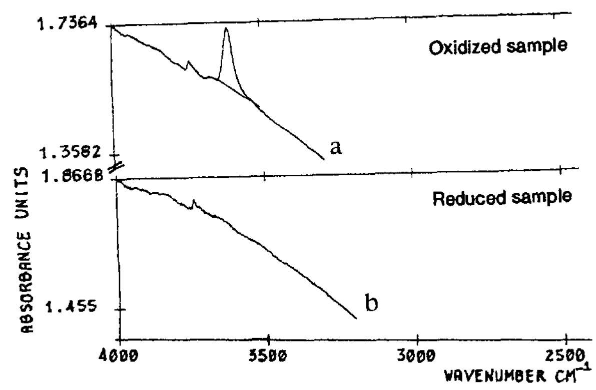

Fig. 2. Infrared spectrum of Ga_2O_3/H-ZSM-5 (Si/Al = 13); (a) after oxidation 873 K, (b) after reduction 873 K.

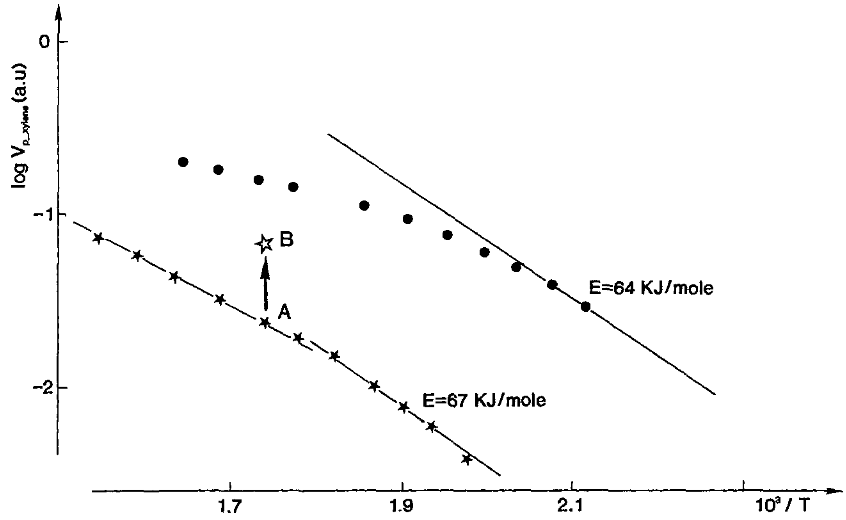

Fig. 3. Isomerization of *m*-xylene over Ga_2O_3/H-ZSM-5 (Si/Al = 60); (●) Ga_2O_3/H-ZSM-5 oxidized 873 K, (★) Ga_2O_3/H-ZSM-5 reduced 873 K.

perature of the reaction increased. The apparent activation energies calculated from the straight lines are given in figs. 3 and 4. From these figures, it appears that it is only relevant to compare the rates in the linear part of the curves, e.g. below 500 K.

It is obvious from the examination of figs. 3 and 4 that in both cases (Si/Al = 13 and Si/Al = 60), the activity of the catalyst was strongly decreased by

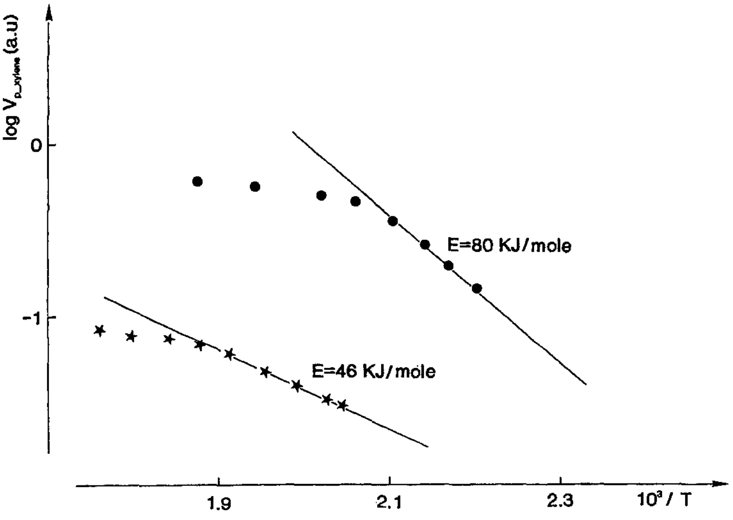

Fig. 4. Isomerization of *m*-xylene over Ga_2O_3/H-ZSM-5 (Si/Al = 13); (●) Ga_2O_3/H-ZSM-5 oxidized 873 K, (★) Ga_2O_3/H-ZSM-5 reduced 873 K.

the hydrogen treatment: a decrease of 20 is obtained at 480 K for Ga/H-ZSM-5 (Si/Al = 13) and of 18 at 500 K for Ga/H-ZSM-5 (Si/Al = 60).

The decrease in apparent activation energy due to hydrogen treatment (see fig. 4) is significant and it could mean either that the gallium ions which have migrated inside the pores are changing the rate of diffusion of *p*-xylene or/and that the few remaining sites responsible for the activity are located deeply inside the zeolite grains, internal diffusion limiting the rate of *p*-xylene formation. For the less acidic sample (Si/Al = 60), the behaviour is slightly different since it is observed that the apparent activation energy is only 64 kJ/mol for the oxidized sample compared to 80 kJ/mol for the previous solid.

SEM studies (micrographs are not given here) indicated that the zeolite (Si/Al = 60) has an average particle size of 3–4 μm compared to 1 μm for the zeolite having Si/Al = 13. Such a difference in sizes explains why the zeolite having the largest grains is much less active than the other zeolite.

As observed for the solid with the largest number of acid sites, Ga_2O_3/H-ZSM-5 (Si/Al = 13), the reducing treatment also reduces the apparent activation energy for Ga_2O_3/H-ZSM-5 (Si/Al = 60) solid, the same explanations are also proposed.

It has been indicated in the experimental section that special care was taken in order to avoid any contamination with H_2O, which could reoxidize the solid with the subsequent regeneration of H^+ acid sites.

In order to illustrate the effect of traces of water in the feed (or in diluent gases), the following experiment was performed: on the reduced solid, which had been reacted with *m*-xylene (fig. 3, experimental point: A), a mixture of water (0.1 kPa) and He (total flow rate 2 ℓ/h) was flowed over the solid for 20 min at 573 K and then the reaction again performed: an increased activity is observed (experimental point B, fig. 3) clearly evidencing the influence of water on the activity of the catalyst. This result indicates that it is of importance to remove water impurities from gas used for treatments and/or reactions.

These results are not in agreement with those reported earlier by Iglesia et al. [7], who, measuring the isomerisation rate of 2-methyl-2-pentene at 448 K, have found no significant change between the oxidized and reduced Ga/H-ZSM-5 solids. Having not used such a test reaction to probe the number of protons of the solids, we are not able to confirm/infirm their report and consequently we cannot discuss these contradictory reports.

4. Conclusions

Comparison by IR spectroscopy of Ga_2O_3/H-ZSM-5 (oxidized form) and of Ga_2O_3/H-ZSM-5 (reduced form) indicates a strong decrease in H^+ number, in agreement with previous reports; similarly, the rate of *m*-xylene isomerisation is strongly depressed following the reducing treatment. Thus, direct correlation between acidity determined by IR of OH groups at RT and H^+ catalyzed reaction exists at 473 K. However, apparently the rate of *m*-xylene isomerisation appeared to be controlled by intracrystalline diffusion on hydrogen reduced Ga_2O_3/H-ZSM-5 because reduced Ga entities migrate within the zeolite channels resulting in the neutralization of the most external H^+ sites and also restricting xylene diffusion within the channels.

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