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MULTINUCLEAR NMR AND CATALYTIC INVESTIGATIONS OF DEACTIVATION OF ZEOLITE H-ZSM-5

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Coke formation and catalyst deactivation by the reaction of methanol over a zeolitic catalyst based on H-ZSM-5 for various stream gases (N_2, H_2 or C_4H_{10}) were studied by ^{13}C CP MAS NMR, ^{29}Si MAS NMR, ^{129}Xe NMR and catalytic test reactions with different stream gases (N_2, H_2, C_4 H_{10}). The rate of deactivation varies in the order $N_2 < H_2 < C_4H_{10}$, which can be explained by cracking of paraffinic, olefinic and alkylaromatic coke deposits under the influence of the hydrogenating properties of the stream gas.

1. Introduction

Carbonaceous residues which are deposited on catalysts during reactions of hydrocarbons are the main cause of catalyst deactivation. Significant efforts have been made to elucidate the problem of coke formation [1,2]. Among the experimental techniques, ^{13}C CP MAS NMR [3,4] is mainly used in these studies and recently the ^{129}Xe NMR technique introduced by Fraissard and Ito [5] was successfully employed to gain insight into the free intracrystalline volume of coked zeolites [6,7]. The present paper emphasizes the influence of the stream gas on the nature of the coke species and on the deactivation of the catalyst.

2. Experimental

The catalyst is H-ZSM-5 based (Si/Al = 80 as determined by chemical analysis of the parent zeolite) and pelletized with Al_2O_3 as binder. Catalytic tests were

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performed in a flow reactor at 670 K at a pressure of 1 MPa of the stream gases N_2, H_2 or n-C_4H_{10} with about 20 g of catalyst and a feed of 1.5 g methanol per gram catalyst an hour. Gas chromatographic analysis of the products was performed in each experiment until the concentration of dimethylether exceeded 5%. The feed was stopped then, the reactor flushed at 700 K with nitrogen to remove the adsorbed products and finally cooled to remove the samples for analysis. The surface areas were determined by measuring the nitrogen isotherms. For the fresh pelletized catalyst we found 265 m^2/g. The amount of coke deposited and the hydrogen-to-carbon ratio of the coke were determined by microanalysis [8].

The xenon adsorption isotherms were determined at 300 K on a classical volumetric apparatus. The amounts adsorbed were expressed in xenon atoms per gram of solid. ^{129}Xe NMR spectra were also obtained at 300 K using a BRUKER CXP 100 spectrometer operating at 24.9 MHz. The resonance frequency of gaseous xenon extrapolated to zero pressure was used as a reference. ^{29}Si and ^{13}C MAS NMR measurements were generally carried out on rehydrated samples, which had been kept in a desiccator for 48 hrs over aqueous NH_4Cl. The experiments were performed at a spinning rate of ca. 3 kHz using a BRUKER MSL 300 spectrometer with a resonance frequency of 59.6 and 75.5 MHz for ^{29}Si and ^{13}C MAS NMR, respectively.

A special procedure was used to obtain an extracted coke sample: the coked catalyst was dissolved at room temperature in 40% hydrofluoric acid, filtered, washed with dichloromethane, and dried [2].

3. Results

In table 1 values are collected for the amount of coke deposits, the decrease in surface area of the catalysts, and the time on stream (until the concentration of

Table 1
The amount of coke deposits, the decrease in surface area of the catalysts, and the time on stream (until the concentration of dimethylether exceeds 5%) for n-butane, hydrogen, and nitrogen as stream gas. The two last lines correspond to catalysts which have been streamed with nitrogen for 130 h, then regenerated with oxygen and n-hexane, respectively, and then streamed with nitrogen again.

Stream gas	Coke content (wt.-%)	Loss of surface area (%)	Time on stream (hrs)
C_4H_{10}	13	25	290
H_2	14	45	260
N_2	7	30	130
H_2 reg. oxygen	13	50	250
N_2 reg. oxygen	10	25	170
N_2 reg. hexane	18	25	270

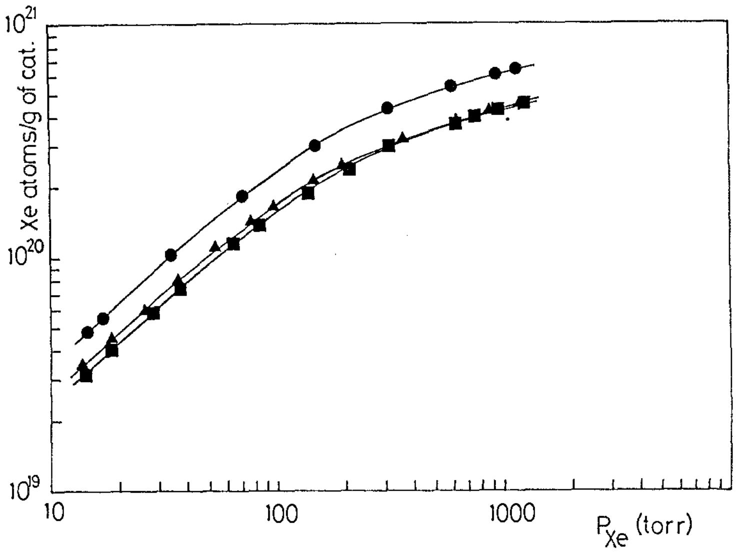

Fig. 1. Xenon adsorption isotherms at 300 K: the fresh catalyst (●); catalyst coked in nitrogen (▲) and hydrogen (■).

dimethylether exceeds 5%) for n-butane, hydrogen, and nitrogen as stream gas. This table shows that the loss of surface area strongly depends on the nature of the stream gas. The atomic hydrogen-to-carbon ratio of the coke deposits of all samples under study is 0.75 ± 0.1.

Fig. 1 shows an important decrease in the amount of xenon adsorbed on samples coked in hydrogen or nitrogen with respect to the fresh sample. At pressures less than 300 Torr, this decrease is comparable with the surface decrease and with the increase in the coke concentration without, however, being proportional to them. The difference for these two samples is small at low pressure and negligible above 300 Torr. All ^{129}Xe NMR spectra show a single symmetrical line. The variation of the chemical shift δ (accuracy ± 2 ppm) as a function of the amount of the xenon adsorbed on the sample (fig. 2) gives two parameters [5]: (i) the chemical shift extrapolated to zero coverage (δ_S) which depends essentially on the average position of the xenon atom and the size of the zeolitic cavities and/or channels; (ii) the slope of the dependence of δ on the amount of the adsorbed xenon which is related to the xenon-xenon interaction in the zeolitic crystallites, that is, to the degree of filling of the void intracrystalline volume. The values of δ_S obtained are similar for fresh and coked samples. Thus, at low concentration, xenon is mainly adsorbed in zones which are not influenced by coke deposits, that is, which do not contain coke. This result shows that coke distribution in the sample is heterogeneous. Fig. 2 shows a greater slope for the coked samples than for the fresh catalyst. This proves that the available free volume is drastically reduced by coke deposition, either by blocking of channels or more probably by deposits in the channel intersections. This last point is confirmed by the fact that

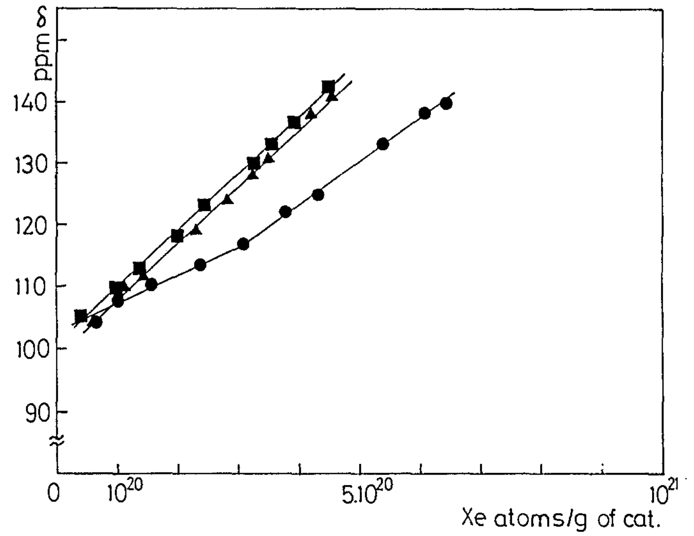

Fig. 2. ^{129}Xe NMR chemical shifts as a function of of sorbed xenon: fresh catalyst (●); catalyst coked in nitrogen (▲) and hydrogen (■).

the change of the slope observed for the fresh sample cannot be observed after coking. On the other hand, the identical curves (fig. 2) for samples with minimum and maximum amount of coke (cf. table 1) show that another portion of the coke must be located outside the crystallites. The signal of xenon adsorbed in the pores of this "external" coke has not been detected, either because of its low concentration or its non-porous nature. Indeed, in order to identify coke porosity one needs a larger amount of porous coke [6].

The ^{29}Si MAS NMR spectra given in fig. 3 show mainly the asymmetrical signal with the peak at −113.5 ppm and the shoulder at −116.8 ppm, which are

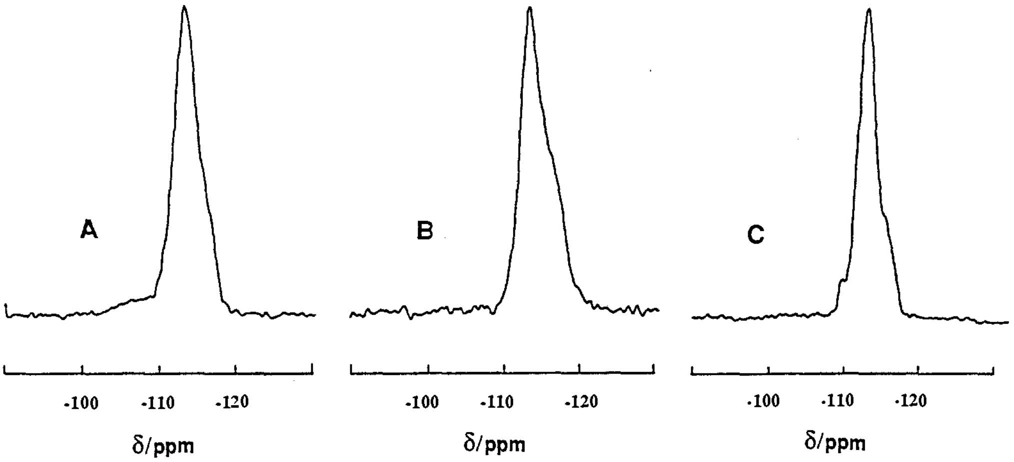

Fig. 3. ^{29}Si MAS NMR spectra of fresh catalyst, A; catalyst coked in hydrogen, B; sample B after regeneration, C.

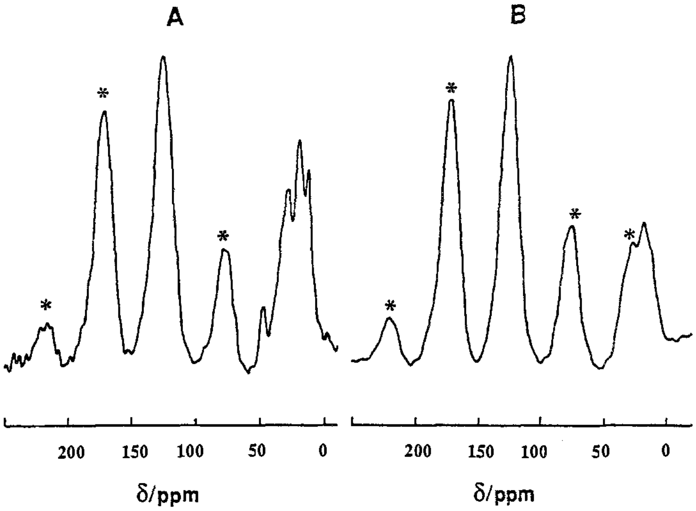

Fig. 4. ^{13}C CP MAS NMR spectra of catalyst coked in n-butane, A; extracted coke deposits, B. The asterisks denote spinning sidebands.

typical for the Si(4Si) grouping in the zeolite ZSM-5 (ref. [9], p. 302). The relatively broad signal at −107 ppm due to the Si(3Si, 1Al) grouping can be only observed in the spectrum of the fresh catalyst (fig. 3A). From the intensity of this line a silicon-to-aluminium ratio of 90 ± 10 can be calculated (ref. [9], p. 212). This line disappears from the spectrum of the sample after time on stream fig. 3B). Taking into consideration the signal-to-noise ratio of the ^{29}Si MAS NMR spectrum the silicon-to-aluminium ratio can be estimated to be larger than 250. This shows that the catalyst framework is dealuminated after time on stream. Also after regeneration of the coked catalyst at 820 K in air no signal at −107 ppm can be observed. The small narrow peak at −109.2 ppm (fig. 3C) belongs to the resolved Si(4Si) signal, which appears in highly siliceous zeolites ZSM-5 (ref. [9], p. 304). Therefore, aluminium cannot be reinserted into the framework by regeneration. It should be noted that ^{27}Al NMR spectra of the samples show principally the signal of the Al_2O_3 binder.

The relative intensities of the ^{13}C CP MAS NMR spectra agree with the values for the coke content. In fig. 4A two bands can be clearly distinguished: the signal at 10–40 ppm due to CH_2 and CH_3 groups and the signal at 120–130 ppm due to aromatic compounds. The ratio of "aromatic-to-aliphatic" intensities is 1.1 ± 0.2, 1.2 ± 0.2 and 2.5 ± 0.2 for samples coked in a stream of N_2, H_2 and C_4H_{10}, respectively.

Fig. 4B shows the spectrum of coke extracted from the catalyst by hydrofluoric acid. Compared to spectrum A, the signal-to-noise ratio is increased whereas the shape of the signal in the aromatic region is not changed.

4. Discussion and conclusion

Coke formation in H-ZSM-5 based catalysts upon methanol reaction is affected by temperature, time on stream, feed composition, pore structure and zeolite acidity [1,2]. Our results show that the nature of coke deposits and the deactivation of the catalyst are significantly different for the various stream gases studied. The rate of deactivation varies in the order $N_2 < H_2 < C_4H_{10}$. The relative amounts of aromatic coke compounds increase in the order $N_2 \sim H_2 < C_4H_{10}$.

The different deactivation rates can be explained by the ability of the monofunctional zeolitic catalyst to activate proton transfer.Therefore, hydrogen as stream gas hydrogenizes and/or hydrocracks paraffinic, olefinic and alkyl aromatic coke deposits, which can be removed after the cracking. The conditions are better with alkanes since hydrogen transfer from alkanes to coke is easier than for the hydrogen molecule.

The evolution of $\delta = f\ \{Xe\}$ curves and the δ_S values show that the coke is heterogeneously distributed. These last results are in agreement with Guisnet et al. [2] and Fraissard et al. [7] who described the formation of coke in two stages: at the beginning molecules adsorbed at the acidic sites cause fast deactivation if they cannot be removed. Most of the reactions forming coke deposits are bimolecular, at least one of the reactants being olefinic [10]. The increase in the coke content during the second stage is the result of the formation of larger size coke species, including a majority of aromatic compounds, but with lower poisoning influence than in stage one.

The dealumination of the zeolitic framework as shown by ^{29}Si MAS NMR is not surprising, since water is a product of methanol conversion and zeolite H-ZSM-5 dealuminates under hydrothermal conditions [11]. Comparing, however the fresh and the oxygen regenerated catalysts (lines 2 and 4 in table 1, respectively) a surprising statement results. While the oxygen regenerated catalysts have a much lower concentration of Brønsted acid sites compared with the fresh catalyst (corresponding to a silicon-to-aluminium ratio of larger than 250 and 80 ± 10, respectively) their catalytic behavior is nearly identical. Both catalysts exhibit the same coke content (14 and 13 wt%) and the same concentration of dimethylether (5%) after being the same time on stream (260 and 250 hrs). Therefore only a small portion of the Brønsted acid sites take part in the catalytic conversion of methanol.

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