JOURNAL OF CATALYSIS **164,** 146–151 (1996)
ARTICLE NO. 0370

Reactivation of Coked H-ZSM-5 by Treatment with Hydrogen and Alkanes

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Received November 27, 1995; revised May 8, 1996; accepted May 29, 1996

The conversion of methanol to hydrocarbons on zeolite H-ZSM-5, in particular the long-term stability of the catalyst, was studied under different reaction conditions. Whereas no significant change in the product distribution was observed, hydrogen and alkane-containing recycle gases show lower deactivation rates than nitrogen. In addition, spent catalysts were partially reactivated by alkane treatment, increasing the time on stream before an oxidative regeneration procedure is required. Lower alkanes such as propane and isobutane yield the best results. The influence of hydrogen-containing gases on the deactivation rate and on the nature of coke on zeolite H-ZSM-5 indicates dissociative adsorption of hydrogen and alkanes on a few sites with enhanced activity. Surface hydrogen species formed by adsorption of alkanes are assumed to make possible the hydrocracking of carbonaceous deposits.

INTRODUCTION

The formation of carbonaceous deposits (coke) on catalyst surfaces causes economic and technological problems in hydrocarbon processing due to loss of activity and changes in selectivity. In the particular case of zeolite catalysts, the formation and the nature of coke have been widely studied (1, 2) and many efforts have been made to reduce the deactivation rate by variation of the reaction conditions and modification of the catalyst. As regards the methanol-to-gasoline (MTG) process, which is our specific concern in this paper, there are numerous reports concerning the effects of the pore structure of the zeolites, the aluminium content and crystallite size as well as the reaction temperature on the coking rate, the location, and the nature of coke species (3). Raising the temperature from 563 to 683 K in the methanol conversion results in a change from hydrogen-rich low-temperature coke to hydrogen-deficient polyaromatic high-temperature coke and reduces the coke content from ∼12 to ∼0.1% (4). In this case the increased reaction temperature does not lead to a more severe deactivation but prolongs the time on stream from several minutes to more than 100 h by converting some of the coke species to volatile molecules. Therefore, the term "coke" should not only include carbonaceous species with a broad range of compositions acting as residues but also deposits which should not be considered as inert end products.

The aim of this work is to investigate the effect of carrier gases on the ageing rate of zeolite H-ZSM-5. The use of hydrogen in acid catalysed reactions is often recommended but relatively few studies concern its influence on the mechanisms of coking and the removal of coke by oxygen-free procedures (5, 6) because on acid catalysts without any metal component the activation of molecular hydrogen is not assumed. However, on strongly acidic zeolites hydrogen transfer reactions have been observed in olefin hydrogenation (7), alkane dehydrogenation (8), and dewaxing of high-pour gas oils (9). In the latter case cofeeding of hydrogen-rich gases as light alkanes gives longer times on stream. On the other hand, in the case of the strongly exothermic methanol conversion it can be expected that the temperature increase and the heat flux out of the small reaction zone depend on the heat capacity of the different carrier gases. A broadening of the reaction zone and moderate temperature profiles within the catalyst bed should result in a longer catalyst lifetime.

EXPERIMENTAL

H-ZSM-5 Zeolite (Si/Al = 80; 2–5 μm particle size) was pelletised with 30 wt% γ-Al_2O_3 as binder. Methanol conversion was studied in two fixed-bed reactors (100 ml and 5 liters of catalyst) with gas recirculation at 640 K (reactor input), variation of weight–hourly–space velocity (WHSV) between 0.9 and 2.0 h^{-1} and at 1.0–3.0 MPa nitrogen and hydrogen. The third carrier gas, rich in light alkanes, was formed by the reaction products after some hours on stream or a commercial propane/*i*-butane mixture. The proportion of recycle gas to the methanol feed was 9–12 $mol_{gas}/mol_{methanol}$. Products were analysed by gas chromatography. The total olefinic content of the products was determined by the amount of bromine (in g) which could be added to 100 g hydrocarbons.

When the gas phase concentration of dimethyl ether exceeded 5% the methanol feed was stopped, and this time on stream was defined as breakthrough or cycle time. After flushing with nitrogen at 700 K samples of coked catalyst

0021-9517/96 $18.00

were removed and characterised by TPO/TG, H/C ratio, ^{13}C and ^{29}Si MAS NMR measurements.

Removal of coke on spent catalysts was achieved by treatment with alkanes at 670–720 K. In the 5 liter pilot scale reactor the procedure consists of stopping the methanol feed at breakthrough of dimethyl ether and recirculating the hydrogen-containing light gases for several hours at reaction temperature. At the end of a cycle in the 100-ml reactor the catalyst samples were processed with hydrogen, a commercial propane/*i*-butane mixture or *n*-hexane at 1.0 MPa. Because it was difficult in both reactors to take out catalyst samples before and after the treatment the changes occurring in coke composition of spent H-ZSM-5 samples by hydrogen or propane/*i*-butane were investigated in a microreactor under normal pressure.

RESULTS

Temperature Profile in the MTG Reaction

It is a characteristic feature of the methanol-to-gasoline process in a fixed-bed reactor that the methanol conversion is completed within a small reaction zone. Because of catalyst deactivation this zone moves through the reactor. The position of the reaction zone within the catalyst bed is indicated by an S-shaped adiabatic temperature rise of about 60 K (Fig. 1) mainly caused by the strongly exothermic aromatization step.

The change of carrier gas did not result in a significant broadening of the reaction zone or a decrease of temperature rise. However, temperatures lower than 610 K at reactor input resulted in shorter times on stream.

The breakthrough time of methanol and dimethyl ether is taken as a measure of the deactivation rate of the catalyst. By recording the temperature profile the appearance of unconverted methanol, i.e., the degree of deactivation, can easily be predicted. A slow shift of the profile indicates a low coking rate.

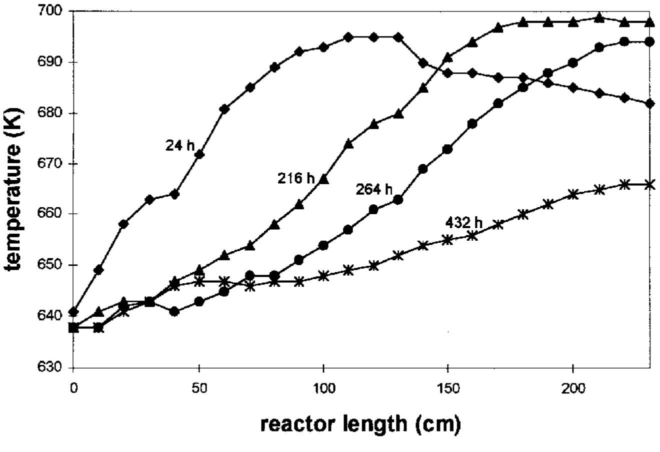

FIG. 1. Temperature profile of the MTG fixed-bed reactor in dependence on time on stream (temperature at reactor inlet, 638–642 K; WHSV, 1.5 h^{-1}; pressure, 1.6–2.0 MPa).

Effect of Time on Stream on Product Distribution

Within the reaction zone an initial product distribution is formed. Depending on the position of the reaction zone i.e., on the amount of fresh catalyst downstream, these products will undergo further conversion. Hence, the product distribution of the MTG reaction changes with the time on stream (Fig. 2). Diffusion limitation in coked zeolites has only minor influence on the variation of the *para* isomer content of xylenes and the *iso*/*n* ratio of alkanes with the time on stream. The closer the reaction zone is to the reactor output, the greater the amount of initial MTG products obtained. Therefore, the increase of olefins with the time on stream results immediately from the reaction mechanism of methanol conversion. Despite coke deposits the rate of olefin isomerization must be high because the *iso*/*n* ratios of pentene and hexene are close to their equilibrium values. On the other hand, in the initial product distribution *iso*-alkanes are clearly the dominant species. This may be related to the stability of the tertiary carbocation formed as intermediates in the methylation of olefins (9).

As with the shifts in the temperature profile, sharp alterations in the olefin content and the *iso*/*n* ratios of paraffins are connected with crucial changes in catalyst activity (Fig. 2).

Effect of Carrier Gas on Time on Stream

As in the case of bifunctional catalysis, the data in Table 1 support the assumption that the reaction atmosphere of the MTG process control deactivation and coke formation on H-ZSM-5. Although no significant differences in the product distribution between the different carrier gases were observed, hydrogen and light alkanes prolong the time on stream more than twofold compared with that seen with nitrogen.

The characterisation of the spent samples shows that the recycle gas influences the deactivation rate via the nature of carbonaceous deposits. ^{13}C CP MAS NMR data and the H/C ratio show a high portion of polyaromatic coke in atmospheres containing light alkanes. The use of a hydrogen atmosphere results in coke with relatively high density and low decrease of catalyst surface compared with coke under nitrogen.

Dealumination during Methanol Conversion

The coke deposits on spent catalysts are usually burned off by an oxygen–nitrogen mixture. H-ZSM-5 zeolites can be used in the MTG reaction for several cycles without significant loss of activity. It often, appears that the second cycle time is longer than the first one (10), although

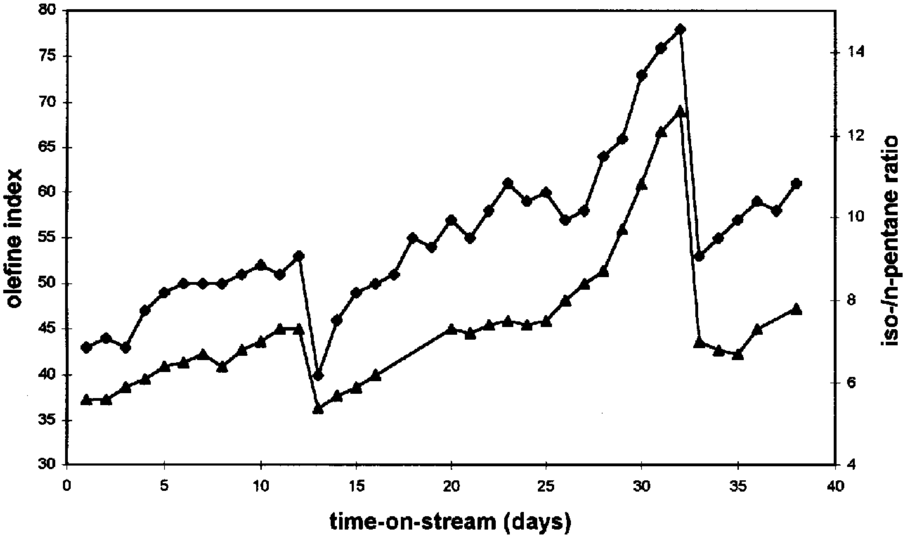

FIG. 2. Content of olefins (◆) and *iso*/*n* ratio of pentanes (▲) in dependence on time on stream (reactivation procedure after 12 and 32 days).

^{29}Si MAS NMR studies show a significant loss of framework aluminium during the first run (Fig. 3).

The signal intensities of the Si(1Al) atoms at 107 ppm and Si(0Al) atoms at 112 ppm indicate that the Si/Al ratio increases from 80 for the parent zeolite sample to values of >400 for the coked catalyst. Compared with H-ZSM-5 samples synthesised with such a low framework aluminium content, the dealuminated zeolites yielded longer times on stream (11). Therefore, the methylation, cracking, and aromatization processes within the methanol conversion on H-ZSM-5 need only a very small number of active sites.

Treatment of Coked Samples with Hydrogen and Alkanes

The assumption of hydrocracking of coke species by hydrogen-containing gases during the MTG process stimulated further regeneration studies. After breakthrough of dimethylether and stopping the methanol feed, the reactor was held at reaction temperature and hydrogen, propane/*i*-butane, and *n*-hexane were tested as hydrogenating agents. Whereas *n*-hexane was fed at WHSV of 1.5 h^{-1} for 4 h hydrogen and the alkane-containing recycle gas were circulated over the catalyst bed for about 12 h.

In all cases, after restarting the methanol feed the position of the temperature maximum in the catalyst bed was shifted towards the reactor input (Fig. 4). Parallel to the shift of the reaction zone the olefinic content of the MTG products and the ratio of *iso*- to *n*-alkanes changed (Fig. 2), indicating a significant reduction of the degree of deactivation by the alkane treatment.

TABLE 1

Characterisation of H-ZSM-5 Zeolite Catalysts Used in Methanol Conversion at 693 K, 1.5 h^{-1} and Different Recycle Gases

	Reaction atmosphere		
	Nitrogen	Hydrogen	Propane/*i*-butane
Time on stream (h)	127	267	290
Coke content (%)	7.4	14.3	13.4
Coking rate ($mg_{coke}/g_{methanol}$)	0.39	0.36	0.31
H/C ratio	0.76	0.82	0.64
^{13}C NMR aromaticity[a]	1.1	1.2	2.5
Loss of BET surface[b] (%)	30	45	25

[a] Ratio of aromatic-to-aliphatic NMR intensities.

[b] BET surface area of fresh catalyst 260 m^2/g.

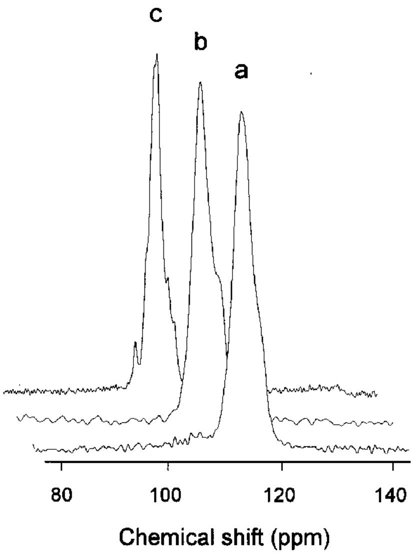

FIG. 3. ^{29}Si MAS NMR spectra of fresh (a), coked (b) and regenerated (c) H-ZSM-5 sample.

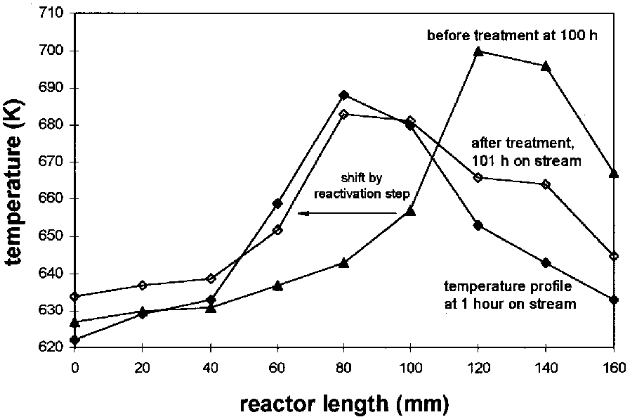

FIG. 4. Temperature profile in the 100-ml catalyst bed before and after a *n*-hexane treatment in the MTG process at 100 h time on stream.

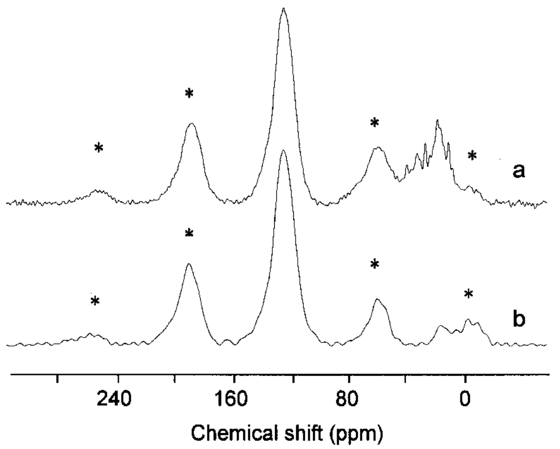

FIG. 5. ^{13}C CP MAS NMR spectra of coked H-ZSM-5 (a) and after treatment with propane (b) (sidebands are marked with asterisks).

The reactivation procedure can be repeated several times but the gain of additional time on stream decreases and the coke has finally to be removed by oxidation. At the end of the pilot scale study the H-ZSM-5 zeolite had converted more than 1500 g methanol/g_{cat} with two recycle gas reactivation steps and was covered with 20.9 wt% coke (H/C ratio = 0.5).

In order to investigate the effect of alkane treatment, samples of spent catalyst were removed and treated with hydrogen and propane/*i*-butane in a microreactor at 693 K under normal pressure for 12 h. Whereas only minor changes in the nature of coke were observed following the treatment with hydrogen, treatment with propane/*i*-butane significantly reduced the amount of coke and increased the content of aromatic species (Table 2). The significant decrease of paraffinic deposits due to alkane treatment is indicated by the low intensities in the 10–40 ppm range of ^{13}C CP MAS NMR spectra (Fig. 5).

The change in the nature of the coke by alkane treatment is also indicated in temperature-programmed oxidation (TPO) studies. The shift of the TPO profile (Fig. 6) to higher temperatures indicates that the H/C ratio of the coke has been reduced by the treatment with propane/*i*-butane. Carbon dioxide evolution reached a maximum at about 830 K for the untreated samples and at about 890 K after reactivation procedures. As may be concluded from the significant loss of weight in the low temperature oxidation range, the decrease of coke content is mainly due to the loss of hydrogen-rich paraffinic species and aliphatic side chains.

TABLE 2

Characterisation of a Spent H-ZSM-5 Catalyst Used in Methanol Conversion (693 K, 0.9 h^{-1}, 740 h Time on Stream) and Treated in a Stream of Propane/*i*-Butane at 693 K for 12 h

	Before treatment	After treatment with propane/*i*-butane
Coke content (%)	13.3	10.2
H/C ratio	0.86	0.69
Loss of surface[a] (%)	23	20

[a] BET surface area of fresh catalyst 310 m^2/g.

DISCUSSION

As demonstrated by Karge *et al.* (12) the reaction temperature has a decisive influence on the nature of coke species. Moreover, when zeolites deactivated at reaction temperatures about 600 K were heated after reaction in a flow of oxygen-free nitrogen up to 700 K, their activity was retained to some extent (13). This partial gain in activity by pyrolysis is expected to be due to cracking of large hydrocarbon molecules which cannot leave the zeolite channels at reaction temperatures. During pyrolysis hydrogen-rich C_1–C_4 fragments diffuse out of the zeolite channels and the

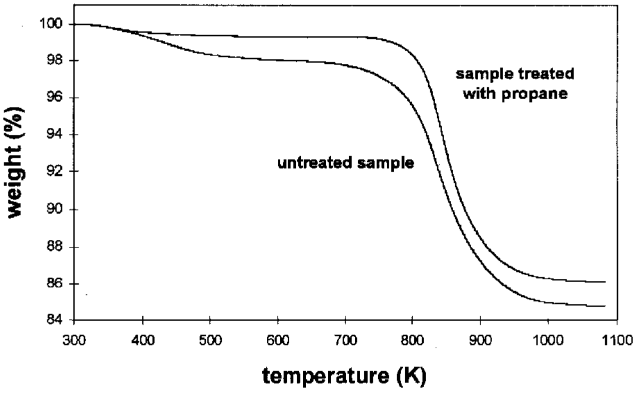

FIG. 6. TPO profile of a coked H-ZSM-5 sample before and after propane treatment.

remaining carbonaceous deposits are highly polyaromatic or graphitic in nature with a low H/C ratio (14). At higher temperatures it is even possible that coke species are remobilised and accumulated on the external surface of zeolite crystallites (3).

In the MTG reaction at about 700 K a high temperature coke is produced. The results of the present investigation demonstrate that the presence of hydrogen and alkanes has a positive effect on the stability of H-ZSM-5 catalysts during methanol conversion. This effect is caused by differences in the rate of coke formation and in the nature of the high temperature coke deposited under the different reaction atmospheres (Table 1).

If the observed rejuvenation of spent samples is not related to impurities of Fe, Ti, and Zr in the ppm range one has to assume that acid zeolites are able to activate hydrogen bonds and facilitate hydrocracking steps of coke, e.g., splitting of alkyl (R) groups from coke species:

$$\text{R-coke} + \text{H}_2 \xrightarrow{\text{H-zeolite},\, T} \text{R-H} + \text{H-coke}.$$

For the desired destruction of long-chain paraffinic coke and the dealkylation of alkylaromatic species, donors of hydrogen atoms are needed. As indicated by longer times on stream (see Table 1), alkanes are more effective as sources of hydrogen surface species than molecular hydrogen.

In the conversion of methanol to hydrocarbons, the zeolite is in constant contact with water. Under these conditions the framework of H-ZSM-5 is dealuminated. The number of remaining sites must be low because they are not detectable in ^{29}Si MAS NMR spectra. On the other hand, these few sites are sufficiently active for complete conversion of methanol over many cycles. It is clear that the formation of the new catalytic sites in zeolites of moderate Si/Al ratios during the MTG reaction are comparable with the generation of enhanced activity sites by mild steaming (15). During the MTG reaction these sites are created at temperatures 100 K lower than is required for steaming. The dealumination and the formation of new sites may be favoured by some oxygenates formed in the MTG process and yielding the acidity of MTG water (pH values of about 3.4). The new sites formed by methanol conversion display enhanced activity in hydrocarbon processing. As Lukyanov (16) has shown for cracking, the hexane conversion increased from 13.7% on the fresh H-ZSM-5 up to 25.4% on the same catalyst after a 35-min-long MTG reaction period.

The enhanced catalytic activity of the new sites is also demonstrated by the formation of molecular hydrogen in the methanol conversion under nitrogen. Considering an adsorbed nonclassical carbonium ion the proton attack at the C−H bond of paraffins and olefins yields an adsorbed alkyl or alkenyl fragment and hydrogen:

$$\text{R-H} + \text{H}^+_{\text{ads}} \rightarrow \text{R}^+_{\text{ads}} + \text{H}_2.$$

The reverse reaction results via hydrogen transfer in reduced amounts of alkenyl and long-chain alkyl ions on the surface. Using coadsorbed isobutane as hydrogen donor Kiricsi *et al.* (17) verified this assumption by UV–vis and IR studies with 1-butene on zeolite La-Beta:

$$\text{R}^+_{\text{ads}} + i\text{-C}_4\text{H}_{10} \rightarrow \text{R-H} + i\text{-C}_4\text{H}^+_{9\ \text{ads}}.$$

Therefore, hydrogen transfer reactions reduce the coking rate by the saturation of volatile olefinic coke precursors. However, it should be noted that these coke species must be located in close proximity to acidic sites. This precondition can only be satisfied for very few coke species. Coke is deposited within the voids throughout the zeolite crystallites and on their surface. Hence, migration of formed hydrogen species on the zeolite surface towards carbonaceous deposits has to be supposed.

The formation of aromatics and carbonaceous deposits during the MTG reaction is a source of hydrogen atoms found in paraffinic products. In addition, polyaromatic coke species may act themselves as centers for hydrogen transfer reactions. Hydrogen atoms from various reactants may be transferred at higher temperatures to polyaromatic structures because of their ability for resonance stabilisation. In a second step, these hydrogen atoms may be added to unsaturated products or transported throughout the carbonaceous deposit (18). Nevertheless, the participation of hydrogen in acidic catalysed reactions needs an acceptable explanation for the activation of molecular hydrogen into charged hydrogen species and for their migration on the zeolite surface.

If heterolytic dissociation of H_2 and alkanes is assumed, then the protons and carbocations are unquestionably associated with the oxygen anions of the framework. As solid-state ion exchange (19) and H/D isotope exchange of OH-groups (20) on zeolites show, the mobility of positively charged particles in zeolites is relatively high:

$$\begin{aligned}\text{H}_2 &\xrightarrow{\text{zeolite}} \text{H}^- + \text{H}^+\\ \text{RH} &\xrightarrow{\text{zeolite}} \text{H}^- + \text{R}^+.\end{aligned}$$

Hydride species, whenever formed, could be stabilised by aluminium atoms at framework distortions (8) or by extraframework aluminium and certainly possess very short lifetimes. Therefore, the migration of hydride species on the zeolite surface and their addition to bulky carbonaceous carbocations may be regarded as low.

The problems with respect to the mobility of hydride species formed by heterolytic dissociation can be avoided by a radical-like dissociative adsorption of hydrogen and alkanes:

$$\begin{aligned}\text{H}_2 &\xrightarrow{\text{zeolite}} 2\,\text{H}^{\cdot\delta+}[\text{zeolite}^{\delta-}]\\ \text{RH} &\xrightarrow{\text{zeolite}} \text{H}^{\cdot\delta+}[\text{zeolite}^{\delta-}] + \text{R}^+[\text{zeolite}^-].\end{aligned}$$

Homolytic dissociation of H_2 and RH into radical cations or positively charged adatoms matches the ionic character of acid catalysis better than the assumption of radicals, but homolysis and radical type transformation in zeolites have to be considered as rather curious at temperatures below 800 K.

On acidic sites on enhanced catalytic activity the adsorption and activation of alkanes may occur via pentacoordinated carbonium ions. The adsorption of hydrogen on such sites,

$$H_2 \xrightarrow{\text{H-zeolite}} H_3^+ [\text{zeolite}^-]$$
$$RH \xrightarrow{\text{H-zeolite}} RH_2^+ [\text{zeolite}^-],$$

may form positively charged H_3 species. Both cations could be considered as relatively mobile and migrate through the voids of the crystallites. The dissociation of these cations in the neighbourhood of carbonaceous deposits yields hydrogen adatoms and a proton or a tricoordinated carbocation. This may explain the hydrocracking of coke species located away from acid sites. Moreover, the explanation includes the assumption that sites which are capable of hydrogen and alkane activation are more resistant in respect of coking than normal catalytic sites of H-ZSM-5.

Results from hydrogen spillover studies on zeolites seem to support this adsorption and migration route. As shown by H–D exchange of the OH group, the surface hydrogen species have a high mobility and the possible charged character of the species is indicated by the influence of a magnetic field on their migration velocity (20).

As isotopic studies with propane/deuterium on HZSM-5 (8) show, the surface hydrogen pool consists mainly of hydrogen adatoms formed from the alkane molecules rather than from molecular deuterium. This implies that all C–H bonds in the alkane are broken by reversible dissociative adsorption before a product molecule is formed. This surface concentration of hydrogen remains largely nonequilibrated with gas-phase dihydrogen and can be used as an effective hydrogen source for the desired hydrogenation and hydrocracking reactions of carbonaceous deposits.

CONCLUSIONS

In the methanol-to-gasoline process the breakthrough of methanol and dimethylether ends the cycle time and the conversion reactor has to be regenerated. By a treatment with alkanes a partial reactivation of coked HZSM-5 zeolites is attained, increasing the time on stream before the combustion of carbonaceous deposits is required. This rejuvenation effect on a coked acid zeolite, free of hydrogenating metal components, can be taken as experimental evidence for dissociative adsorption of hydrogen and alkanes. Due to the additional time on stream and the decrease of coke content, alkanes are an excellent hydrogen source for the hydrocracking of alkylaromatic coke species.

At the end of the first cycle a strong dealumination of the used zeolites was observed. However, this loss of framework aluminium did not cause any decrease of activity and stability in the following cycles. Therefore, H-ZSM-5 zeolites of moderate Si/Al ratio used in the methanol-to-gasoline reaction show enhanced activity in hydrocarbon processing in the same way as zeolites treated by mild hydrothermal processes.

ACKNOWLEDGMENTS

The authors acknowledge with thanks the assistance of Dr. W. Geyer (Leipzig) with the TPO experiments and express their gratitude to the Deutsche Forschungsgemeinschaft for supporting these investigations.

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