JOURNAL OF CATALYSIS **136**, 258–262 (1992)

Isotope Exchange of Coke Hydrogens for Deuterium of Various Organic Compounds: Studies of Coke Deposited on a HZSM-5 Zeolite in Acetone Conversion

Coke residues on catalysts have been investigated on the basis of chemical composition, location, poisoning function, and removal conditions (*1–3*). Less attention has been paid to the reactivity of the individual coke components of which carbon and hydrogen are predominant. This contribution concerns the ability of coke hydrogens to be exchanged at 300°C for the deuterium of perdeuterated organic compounds, namely ethylene, propene, and benzene. Some experiments were also carried out with toluene, ethylbenzene, and naphthalene to broaden the range of kinetic diameters of the reacting molecules. The number of exchanging hydrogens of coke and the reaction kinetics was compared with those of the hydroxyl hydrogens of the parent uncoked zeolite.

HZSM-5 zeolite (Si/Al = 13.6) was prepared from the Na form (supplied by the Research Institute for Oil and Hydrocarbon Gases, Czechoslovakia) by acid leaching and was pretreated prior to the catalytic measurements at 450°C in a helium stream. It was coked in acetone conversion (350°C, 70 vol% of acetone in a helium stream, weight–hour–space velocity 5 h^{-1}, 25 g of acetone passed over 1 g of zeolite), so that the initial sorption capacity 5.2 mmol g^{-1} decreased to the value of 0.1 (measured by Ar adsorption at −195°C); the zeolite contained 10.7 wt% of coke with H/C ratio = 1.49 (*4, 5*). This sample was designated as completely coked, and, in some cases, was pyrolyzed in a vacuum at 600°C and/or partially oxidized at 500°C in a 20% oxygen/helium stream.

The perdeuterated compounds (99.5–99.8 at.% enrichment, supplied by the USSR) were employed without any purification. They were: ethylene, propene, and benzene and in some cases also toluene, ethylbenzene, and naphthalene.

All the samples (0.1 g) were pretreated in a vacuum (10^{-4} Pa) at 300°C in an apparatus connected via a fine needle valve to a Finnigan 400 quadrupole mass spectrometer. The volume containing the sample (500 cm^3) was filled with the deuterated compound (80–230 Pa, except naphthalene whose pressure was 15 Pa) and the isotope exchange was measured at 300°C by admitting a negligible part of the gaseous phase into the mass spectrometer. The spectra were usually recorded with low ionization energies to obtain the molecular peaks.

A typical course of the isotope exchange (IE) kinetics of deuterium for the reactants studied for the hydrogen of the hydroxyl groups of HZSM-5 zeolite and of coke in HZSM-5 is exemplified by C_2D_4 exchange in Fig. 1: (a) the atomic deuterium concentration vs time plot, (b) the $\ln(1 - F)$ vs time plot (for F see the legend under Table 1). It can be seen that the IE reaches an equilibrium value within a very short time interval for the OH groups of the parent, uncoked sample, while for H of coke it takes many hours. The exponential law is obeyed only in the former case (Fig. 1b). The rates of IE on both the coked and uncoked zeolites for perdeuterated ethylene, propene, and benzene are listed in Table 1. For the coked samples, the rates were calculated using the initial IE values; taking into account all the coke hydrogens (the IE after 24 h included at least 80% of all hydrogens present in the coked samples), the rates are two to seven times lower than the IE rates on the uncoked

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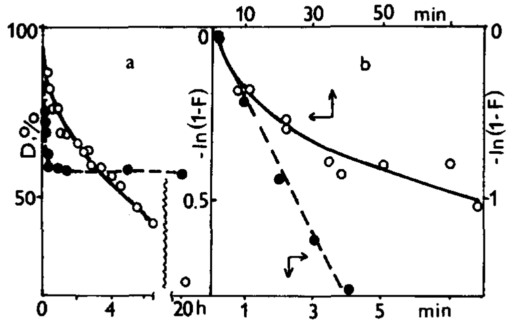

FIG. 1. Kinetics of the isotope exchange of C_2D_4 with HZSM-5. (a) D, at.% vs time plot, (b) $-\ln(1 - F)$ vs time plot; $F = (c_0 - c_t)/(c_0 - c_\infty)$; c_0, c_t, and c_∞ are deuterium concentrations at the relevant times. (○) Coked zeolite, (●) parent zeolite.

zeolite with hydrogens of the OHs (Table 1). The determination of the linear region of the logarithmic dependence is somewhat arbitrary with coked samples. Nevertheless, considering the various reactant pressures, the IE rate of ethylene is the lowest one. This agrees well with our previous results on IE of various deuterated reactants for hydrogen of hydroxyls of less acidic HY zeolites (*6*). The majority of acid centers on coked HZSM-5 is occupied by coke and thus this coked HZSM-5 exhibits lower acidity than the uncoked sample. It can be assumed that on highly acidic uncoked HZSM-5 the intermediate necessary for the IE is formed more easily than on a HY zeolite. This also agrees with the easy oligomerization of ethylene on HZSM-5 zeolite, while on HY zeolite some Lewis acid sites must be present together with acid hydroxyls to initiate the oligomerization. A very rapid IE rate was also found between OHs of uncoked HZSM-5 and perdeuterated naphtalene. This can be understood assuming that not the diffusion of reactants toward the zeolite hydroxyls governs the reaction rate, but that the exchange proceeds in the surface and near-surface layers of the zeolite and that the hydrogens of all inner hydroxyls are jumping very rapidly to the organic reactants and are exchanged for their deuterium. For that reason, the first-order law (Fig. 1b) holds for the exchange between the hydrogen of hydroxyls and the deuterium of the organic compound, even those whose dimensions exceed the pore size of HZSM-5.

The deviation from the first-order kinetic law in the IE of the coked HZSM-5 may be a result of the heterogeneity of the coke hydrogens or of the retarding effect of diffusion (clearly not of reactants whose dimensions do not allow the pores filled with coke to enter, but of hydrogens, either those of coke or those of hydroxyls) through the coke deposit. Both these effects can be expected and neither of them can be excluded on the basis of the simple kinetic data. The heterogeneity of hydrogens can arise from the heterogeneity in the coke alone. However, this does not seem to be very probable for the following reasons: (i) The pyrolyzed

TABLE 1

Rates of Isotope Exchange (R) of Deuterated Reactants at 300°C for Hydrogens of OH Groups and Coke Components on HZSM-5 Zeolite

Reactant	Pressure (Pa)	$R \times 10^{-20}$, parent HZSM-5 (atoms min^{-1} g^{-1})	$R \times 10^{-20}$, coked HZSM-5 (atoms min^{-1} g^{-1})
C_2D_4	226	1.4	0.2
C_3D_6	149	1.0	0.5
C_6D_6	80	0.8	0.4

Note. $R = -\ln(1 - F)\cdot(D + M)/t(D + M)$; D and M are the numbers of hydrogen atoms in the gas and solid (coke and OH) phases, respectively; $F = (c_0 - c_t)/(c_0 - c_\infty)$; c_0, c_t, and c_∞ are deuterium concentrations at the relevant times.

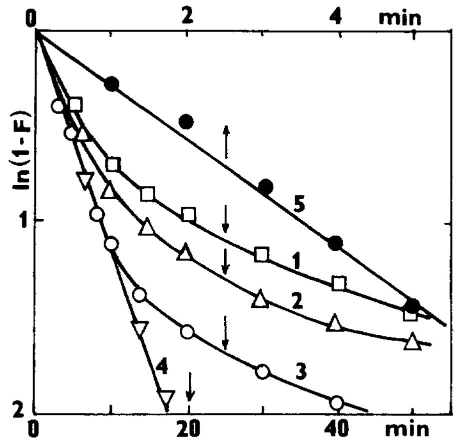

FIG. 2. Kinetics of the isotope exchange of C_6D_6 with HZSM-5. Curves: 1, coked sample; 2, pyrolyzed sample 1; 3, short oxidation of sample 1 (9.7 wt% of coke remains unoxidized); 4, longer oxidation of sample 1 (5.5 wt% of coke unoxidized); 5, parent zeolite.

coke exhibits the same deviation from the exponential kinetic law (see Fig. 2) and the same exchange rate (Table 2) in spite of a substantial change in its character (decreased H/C ratio from 1.4 to 0.7 due to hydrogen removal, disappearence of alkyl substituents on the aromatic rings, and condensation of aromatics), and (ii) partial oxidation would most probably remove the less firmly bound coke hydrogens that should exhibit a higher IE rate, so that, after their removal, a decrease in the IE rate can be expected, but the opposite is true (Fig. 2, Table 2). Unless the heterogeneity of the coke hydrogens is the IE rate-retarding effect, the different rate of the hydrogens of OHs and of coke could play a role. This effect cannot be significant on the completely coked zeolite as the number of coke hydrogens considerably exceeds that of hydroxyls (6.9×10^{21} vs 6.8×10^{20} H atoms per g of dry zeolite, respectively) and, moreover, only about 3% of the bridging hydroxyls remains accessible after complete coking (from 17% of those unoccupied by coke; see Table 2 and unpublished results). In the linear region of the logarithmic dependence about 2×10^{20} H atoms are involved in the IE, so that the possible different exchange rate of OHs and coke hydrogens cannot be (or cannot be completely) responsible for the deviation from the exponential kinetics on coked HZSM-5. This does not mean that the exchange rates of both kinds of hydrogens are the same—if the mixing of hydrogens between hydroxyl groups and coke residues is more rapid than the exchange itself, their heterogeneity does not influence the IE rate. Such an example was reported in

TABLE 2

Rates of Isotope Exchange (R) of C_6D_6 at 300°C for Hydrogens of Completely Coked, Pyrolyzed, and Partially Oxidized HZSM-5 Zeolite

wt% of coke	H/C in coke	$R \times 10^{-19}$ (atoms min^{-1} g^{-1})	Free bridging OH sorption capacity	
			(%)	(Ar, mmol g^{-1})
10.7	1.4	3.7	17[a]	0.1
9.2[b]	0.7	3.6	21[a]	0.2
9.7[c]	0.5[d]	4.6	37	2.2
5.5[c]	0.3[d]	6.1	68	3.7
0	—	8.0	100	5.2

Note. Free bridging hydroxyls were determined from the intensities of the IR band at 3610 cm^{-1}.

[a] OH mostly inaccessible (except 3%) for benzene at room temperature (Kubelková, private communication).

[b] Pyrolyzed at 600°C in vacuum.

[c] Partially oxidized at 500°C in an O_2/He stream.

[d] Calculated from the equilibrium IE value.

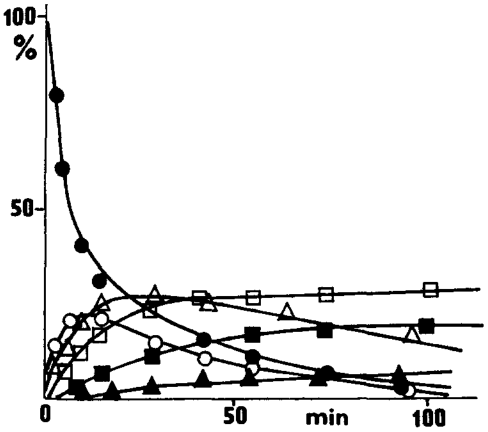

FIG. 3. Individual isotope species of benzene during the exchange with coked HZSM-5. (●) C_6D_6, (○) C_6H_6, (△) C_6H_5D, (□) $C_6H_4D_2$, (■) $C_6H_3D_3$, (▲) $C_6H_2D_4$.

Ref. (7) for two different types of OH groups in HY zeolite, which exchanged their hydrogen at the same rate.

The role of diffusion (resulting in the deviation from the first-order law kinetics) in the IE on coked HZSM-5 is supported by the following points: (i) The very low sorption capacity of the completely coked sample (Table 2) does not allow Ar molecules to penetrate inside the zeolite, so that it is even less probable for ethylene, propene, and benzene with higher kinetic diameters (0.39, 0.49, and 0.66 nm, respectively) than that of Ar (0.34 nm); and (ii) during the partial oxidation, when the pore reopening proceeds, the interval of the linear logarithmic time plot increases and similarly the IE rates also increase (Table 2 and Fig. 2). As the diffusion of reactants cannot be responsible for the effects observed, from the above reasons, the limited movement of OHs hydrogens through the coke is assumed to explain the experimental results.

In Fig. 3, the more detailed isotope reaction path is shown for benzene (the time plot of concentrations of the individual isotope species): it can be seen that during one stay on the surface, the exchange of all six hydrogens occurs, and gradually, as the solid becomes deuterated, the more deuterated species appear in the gaseous phase. The same exchange mechanism was observed for propylene and naphthalene, while for ethylene, only one hydrogen atom is exchanged in one reaction step. These "mechanisms" of the isotope exchange cannot be directly related to the nature of the surface intermediate. In the case of ethylene, a shorter "stay" of the molecule on the zeolite might be caused by a weaker ethylene–zeolite bond, lower ethylene basicity, and therefore lower probability of H transfer from zeolite to ethylene (*6*).

With the exception of benzene (and probably naphthalene), the catalytic conversion of a small part of the reactants occurs, but the extent of the reaction does not affect the isotope exchange. The isotope exchange of gaseous deuterium at 300°C was not found.

The hydrogens of coke are able to undergo isotope exchange with deuterated compounds at the relatively mild temperature of 300°C so that they are not firmly bound in a rigid coke structure. All (or most of) the hydrogens of coke are exchanged, but contrary to the exchange of OH groups of the parent uncoked zeolite, the reaction kinetics are strongly retarded and deviate from the first-order law. The rate-reducing effect is most probably caused by the limited diffusion through the coke. From a sterical point of view, the diffusing species are the H atoms of the OH groups, which mediate the exchange and not the molecules of organic compounds.

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J. NOVÁKOVÁ
L. KUBELKOVÁ

J. Heyrovský Institute of Physical Chemistry
and Electrochemistry
Czechoslovak Academy of Sciences
Dolejškova 3, 182 23 Prague 8
Czechoslovakia

Received June 19, 1991; revised January 28, 1992