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The Effect of Oxygen on the Conversion of Light Paraffins on ZSM-5 Zeolites

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The oxygen effect in the conversion of ethane, propane, and *n*-butane to aromatics using two H–ZSM-5 zeolites with different Si/Al ratios is studied. The presence of small amounts of gas-phase oxygen increases benzene–toluene–xylene formation, in particular at the lower reaction temperatures (below 773 K). The enhancement factor compared to anaerobic activity is higher for the less reactive alkane (ethane) and for the less active zeolite (Si/Al = 164) which also shows the lower total oxidation activity. The formation of carbon oxides decreases considerably when the surface acidity is inhibited by potassium exchange, and the K zeolite is active only in the oxidative dehydrogenation of the alkane. However, it was found that the aerobic activity of the zeolite is also correlated to surface acidity. It is suggested that the main oxygen effect is in the first stage of alkane activation, enhancing the formation of the corresponding olefin. The creation of new active sites was attributed to the interaction of oxygen with solid-state defects forming very reactive oxygen free radical species. Their activity, however, is inhibited during reaction due the formation of carbonaceous residues. © 1989 Academic Press, Inc.

INTRODUCTION

Strong incentives are present today for developing new and/or improved catalysts for the selective conversion of light paraffins. There are two main directions of research: (i) direct one-stage conversion of light alkanes (principally, propane) to aromatics on modified zeolites (*1–9*) and (ii) the functionalization in the presence of oxygen on transition metal oxides (*10–18*). Significant improvements have been made in the first approach by the introduction of Ga-, Zn-, and/or Pt-modified zeolites of the pentasil family (*1–9*), but the reaction conditions are still severe (around 870 K) and good results are obtained only with propane. Catalytic performances (in particular, activity) drastically worsen when lower alkanes such as ethane and methane are used. On the contrary, very active sites form in the presence of gaseous oxygen or other oxidizing agents such as N_2O (*10–16*). These sites are able to activate paraffinic C–H bonds selectively at low temperatures (around 670 K for methane). Good selectivities to products of partial oxidation (for example, methanol and formaldehyde from methane (*10–13*)) may be obtained only at low conversions. With increasing hydrocarbon conversion, carbon oxides are usually obtained as the only products of reaction due to the high reactivity of these products. However, one may expect that if the products of partial oxidation further react giving less reactive molecules, a significant increase in the selectivity is possible (*17*). Zeolite catalysts such as ZSM-5 are well-known systems able to perform the selective transformation of oxygenated products (e.g., alcohols, ethers, aldehydes) (*18*) to hydrocarbons/aromatics with higher carbon atom numbers. The design of a catalytic system where the redox transition metal (selective in the activation of light alkanes in the presence of oxygen) is placed inside a pentasil zeolitic structure (in order to quickly transform the oxygenated prod-

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ucts formed to aromatics) is of potential interest because such a system would offer the advantages of combining the individual activity characteristics of transition metal oxides with the improvement in the selectivity resulting from the zeolitic properties.

Some other possible effects may be expected from the presence of gaseous oxygen: (i) the rate of catalyst deactivation by coking and (ii) the stoichiometric constraint imposed by the hydrogen content of the feed (*5*) may be substantially reduced. Low alkanes are much higher in hydrogen content with respect to aromatic products. The proposed mechanism of formation (*2, 5, 19, 20*) involves a key step of hydrogen transfer from intermediate cyclic or oligomer hydrocarbons and light olefins leading to aromatics and alkanes. According to Engelen *et al.* (*7*) the hydrogen released by the reaction is fully used for the hydrogenation and hydrogenolysis, and the H/C ratio does not change during reaction. The reaction of hydrogen with oxygen to give water is thus expected to modify significantly this proposed mechanism.

The properties of zeolitic catalysts in the conversion of alkanes in the presence of oxygen, however, have been rarely reported in the literature (*21*), although the use of O_2 or N_2O in the production of aromatic hydrocarbons from lower alkanes has been patented (*22*). Anderson and Tsai (*23*) have studied the nitrous oxide oxidation of methane over ZSM-5 and found the formation of methanol/formaldehyde and aromatic products. In an investigation of the oxidative synthesis of aromatic hydrocarbons from propane on pentasil zeolite catalysts Shepelev and Ione (*24*) found an increase in the formation of aromatics and a decrease in the content of methane, ethane, and butane in the presence of O_2. The oxidative heterogeneous catalytic properties of zeolites in the presence of molecular oxygen have been reviewed by Tagiyev and Minachev (*25*). In a recent note Otsuka and Komatsu (*26*) have reported the formation of aromatic hydrocarbons from methane and oxygen using modified zeolites. Oxygen has been used in order to prove a radical reaction mechanism in the transformation of methanol to aromatics on H–ZSM-5 (*27*).

It seems, therefore, from the literature data that unmodified zeolite catalysts already possess oxidative heterogeneous catalytic properties in the conversion of light alkanes in the presence of gaseous oxygen. Within the framework of the previously discussed objective of investigating oxidative heterogeneous catalytic properties of zeolitic-based materials, the aim of the research reported in this paper was to study in more detail the modifications in the mechanism of the conversion of light paraffins on unmodified H–ZSM-5 induced by oxygen in the inlet reactant mixture. In particular, reaction temperatures lower than 723 K were investigated, in order to look for evidence of the activating effect of the oxygen and avoid contributions due to homogeneous or wall reactions.

EXPERIMENTAL

Catalysts. The catalysts used were H–ZSM-5 zeolites with Si/Al atomic ratios of 35 and 164, prepared according to a standard patented method (*28*) (Si/Al = 35) and a modified preparation method (*29*) (Si/Al = 164). The synthesized materials, calcined in air at 773 K for 24 h, were then converted to the H form by ion exchange. The samples were protonated using 1 *M* NH_4Cl solution (50-fold excess) and filtering. This was protonated three times whereupon the samples were washed, dried, and finally calcined in air for 24 h at 843 K. The final degree of ion exchange was more than 98%. The authenticity and crystallinity of the ZSM-5 zeolites was checked by X-ray diffraction and infrared spectroscopy (skeletal vibrations). Chemical composition after ion exchange was determined by atomic absorption and flame photometry. K–ZSM-5 (Si/Al = 164) was prepared from the corresponding H form by ion exchange with KCl using the same procedure as that for NH_4^+ exchange, except for a lower final temperature of calcination (673 K). The preservation of the crystallinity and of the Si/Al ratio after this procedure was checked by X-ray diffraction, infrared spectroscopy, and chemical analysis. The degree of K exchange was more than 95%. For the catalytic tests the zeolites were pressed, crushed, and sorted into grains of 0.3–0.6 mm without any binding material.

Apparatus and reaction method. The conversion of light paraffins was carried out using an isothermal downflow 316 S.S. reactor (i.d. 16 mm, length 550 mm) under atmospheric pressure. A centrally located thermocouple sliding inside an axial tube allowed control of the isothermicity of the axial temperature profile in the catalytic bed (usually 1 g). The reactor was placed inside a copper bar electrically heated externally. Capillary resistance flow meters were used to measure two independent flows of calibrated percentages of hydrocarbon in helium and oxygen in helium supplied from cylinders. The two reactant flows were mixed in a preheater maintained at 473 K and then sent to the reactor through a sampling valve for the analysis of the reactant composition.

The reaction products were analyzed using two on-line gas chromatographs, the first with a flame ionization detector for analyses of organic products and the second with a thermal conductivity detector for analyses of O_2, CO, and CO_2 (the methane peak was used as an internal standard between the two gas chromatographs). The second GC operated with a Carbosieve-II column under programmed temperature control (8 min isothermal at 298 K, then heating to 498 K at 32 K min^{-1}). The first GC used different columns with programmable insertion (Porapak QS operating under programmed temperature conditions from 343 to 493 K, dimethylsulfolane operating under isothermal conditions at 298 K, and 23% SP-1700 on Chromosorb P AW under isothermal conditions at 343 K) for the analysis of saturated, olefinic, and aromatic hydrocarbons or of possible O-containing products. Tests were made on the condensed liquid products using different columns specifically for aromatic separation in order to confirm the results.

The inlet reactant composition was 20.3% (v/v) hydrocarbon, and oxygen was in the 0–10.4% range with a helium flow rate of 60×10^{-3} liter min^{-1}. The normalized amounts of product were calculated on a carbon basis as

Norm. moles h^{-1} = (moles h^{-1} of product) × (number of C atoms in the molecular formula)/(number of C atoms in the starting alkane).

All the data, if not otherwise specified, refer to the catalytic results after 1 h on stream.

RESULTS

Propane

The effect of reaction temperature in the 573–773 K range on the distribution of normalized products in propane oxidation under aerobic and anaerobic conditions is reported in Fig. 1. For higher reaction temperatures it was noted that a substantial contribution due to wall reactions altered the experimental data especially in the presence of gaseous O_2. Due to the presence of deactivation phenomena all the reported data refer to the catalytic behavior exhibited after 1 h on stream. A significant modification of the catalytic activity was noted in the presence of gaseous O_2. In addition to the formation of carbon oxides, the formation of the aromatic (benzene–toluene–xylene, hereinafter called BTX), propylene (C_3^{2-}), and C_4 fractions (the normal-to-iso ratio is around equimolecular) increases significantly. On the contrary, less significant variations in the formation of C_2 (the ethane-to-ethylene ratio is about equal to one) and methane were observed. In both the C_4 and the BTX formation, a clear variation in the trend against the reac-

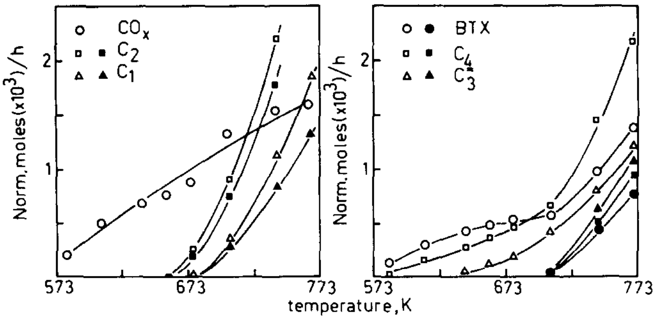

FIG. 1. Effect of reaction temperature on the normalized product distribution in propane conversion on H-ZSM-5 (Si/Al = 35). Oxygen concentration 0.0% (solid symbols), 10.4% (open symbols).

tion temperature is present at around 700 K, in correspondence with the beginning of the activity of the zeolite in the absence of gaseous oxygen.

When the Si/Al atomic ratio in the H-ZSM-5 zeolite was increased from 35 to 164 (Fig. 2) the catalytic activity in the absence of gaseous oxygen drastically decreased, especially as regards BTX formation which is practically zero for temperatures lower than 773 K. On the contrary, a higher BTX formation is observed in the presence of gaseous O_2. However, the yield is lower than that for the zeolite with a higher Al content (Fig. 1). It is worth noting also that the formation of carbon oxides is cut in half at the lower Al content in the zeolite and the C_4 formation decreases considerably. When the H-ZSM-5 (Si/Al = 164) was re-exchanged with potassium in order to inhibit the surface acidity of the zeolite, as expected, no BTX formation and traces of cracking activity were observed under aerobic conditions. The zeolite selectively forms only propylene (Table 1) and, at a much lower rate, carbon oxides. Compared to the results with H-ZSM-5 (Fig. 2), at 770 K the rate of propylene formation decreases around 50 times and that of carbon oxides formation about 130 times. This is evidence that the aerobic activity of the H-ZSM-5 may not be attributed to surface contamination by transition metals. The oxidation activity is rather stable and no change in the rate of propylene and carbon oxides formation on the K-ZSM-5 was observed during about 8 h of catalytic tests.

The oxygen dependence of the BTX formation from propane on the two H zeolites is shown in Fig. 3 where the normalized formation of benzene, toluene, and xylenes as a function of the O_2 concentration in the

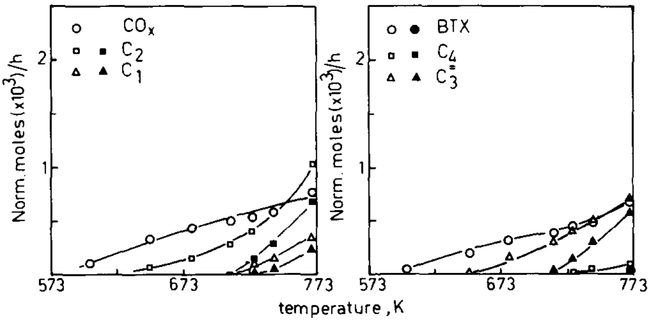

FIG. 2. Effect of reaction temperature on the normalized product distribution in propane conversion on H-ZSM-5 (Si/Al = 164). Oxygen concentration 0.0% (solid symbols), 10.4% (open symbols).

TABLE 1

Effect of Reaction Temperature on the Normalized Formation of Propylene and Carbon Oxides during Propane Conversion on K–ZSM-5 (Si/Al = 164)

Temp. (K)	Propylene	Carbon oxides
	(normalized moles/h)	
674	0.10×10^{-4}	—
685	0.28×10^{-4}	Traces
709	0.70×10^{-4}	1.9×10^{-5}
741	0.05×10^{-4}	3.5×10^{-5}
770	1.41×10^{-4}	6.4×10^{-5}

Note. Oxygen concentration = 10.8%.

inlet reactant mixture is reported. The presence of O_2 does not greatly modify the relative ratio of the three aromatics but considerably increases the absolute quantities formed. The enhancing effect is particularly evident for the zeolite with lower Al content and therefore lower activity in the absence of oxygen. The increase in aromatization activity is particularly significant up to around 2% of oxygen concentration. With further increases in oxygen concentration the BTX formation increases at a much slower rate.

Reported in Table 2 are the oxygen and reaction temperature effects on the H/C ratio in the outlet stream (not considering the carbon oxides and unreacted propane—only traces of H_2 were detected) during propane conversion on H–ZSM-5. The H/C index is useful in order to ascertain the effect of oxygen as a hydrogen acceptor in the aromatization mechanisms. Under anaerobic conditions, the outlet ratio was near that of the inlet reactant (H/C propane = 2.66). In the presence of gaseous oxygen, a decrease in the outlet H/C ratio was observed for both H–ZSM-5 zeolites. It is reasonable to attribute the decrease in the outlet H/C ratio to the formation of H_2O due to oxidative dehydrogenation. The detection of the water deriving from this reaction, however, is masked by that derived from the combustion reaction (formation of CO_x + H_2O). The effect was particularly evident at low reaction temperatures (678 K), where the activity of the zeolite under anaerobic conditions is practically zero. Under these conditions, the outlet H/C ratio was near the value of propylene (H/C propylene = 2.0). For higher reaction temperatures, the outlet H/C ratio increased especially for the zeolite with the higher Al content, showing higher activity under anaerobic conditions.

Figure 4 shows the effect of the time on stream on the aromatic formation from propane under aerobic and anaerobic conditions. The aromatization activity of the zeolite decreases at a much higher rate under

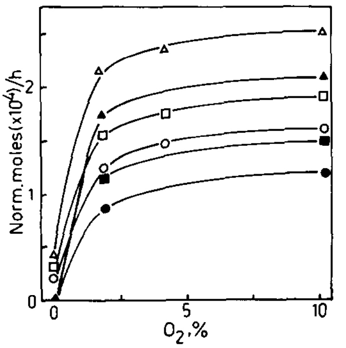

FIG. 3. Effect of oxygen concentration in the inlet reactant mixture on the normalized formation of aromatics from propane at 693 K on H–ZSM-5 with Si/Al = 35 (open symbols) and Si/Al = 164 (solid symbols). (□, ■) Benzene, (▲, △) toluene, (○, ●) xylenes.

TABLE 2

Effect of the Presence of Oxygen and of Reaction Temperature on the H/C Ratio in the Outlet Hydrocarbon Stream (Not Considering Carbon Oxides and the Unreacted Propane) during Propane Conversion on H–ZSM-5 Zeolites

Reaction temp. (K)	O_2 (%)	Si/Al	Outlet H/C
678	0	35	2.62
678	10.4	35	1.97
678	10.4	164	1.94
743	0	35	2.56
740	0	164	2.55
743	10.4	35	2.42
740	10.4	164	2.16

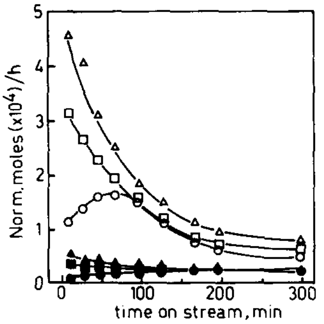

FIG. 4. Effect of time-on-stream on the formation of aromatics from propane at 693 K on H-ZSM-5 with Si/Al = 35 in the presence of gaseous oxygen (10.4%, open symbols) and in the absence of O_2 (solid symbols). (□, ■) Benzene, (▲, △) toluene, (○, ●) xylenes.

aerobic conditions than in the absence of gaseous oxygen. After around 10 h the aerobic activity becomes practically equivalent to that in the absence of O_2. The activity, both under anaerobic and aerobic conditions, may be regenerated, however, by oxygen treatment at higher temperatures (823 K). The formation of benzene and toluene decreases at approximately the same rate, whereas the xylene formation shows a maximum in the rate of formation. This suggests a possible consecutive formation of xylenes through a mechanism involving carbonaceous materials formed during the deactivation process.

Ethane and n-Butane

Due to the reduced contribution of anaerobic activity, the oxygen effect on the ethane and *n*-butane aromatization was studied using only the H-ZSM-5 zeolite with Si/Al = 164.

The effect of reaction temperature on the normalized product distribution in ethane oxidation under aerobic and anaerobic conditions is reported in Fig. 5. The activity is practically zero in the absence of gaseous oxygen (only small amounts of ethylene and methane are formed at the higher temperatures). The presence of oxygen in the feed drastically increases the formation of all products, particularly ethylene and BTX. It is worth noting that C_5 hydrocarbons form with higher yields than those of the propane conversion under the same conditions.

Figure 6 shows the effect of the oxygen concentration in the inlet reactant mixture on the normalized formation of aromatics from ethane. As in the case of propane, the increase is particularly marked up to around 2% oxygen concentration and a further oxygen increase only slightly modifies the aromatization activity. However, contrary to that found for propane, toluene and xylenes are the principal aromatics and little formation of benzene is observed. This is in contrast with that reported by Inui *et al.* (*1*) who, when working under anaerobic conditions, found a significant formation of benzene from ethane at higher reaction temperatures. However, our results agree with those reported by Védrine *et al.* (*20*) in a study of the conversion of ethylene on

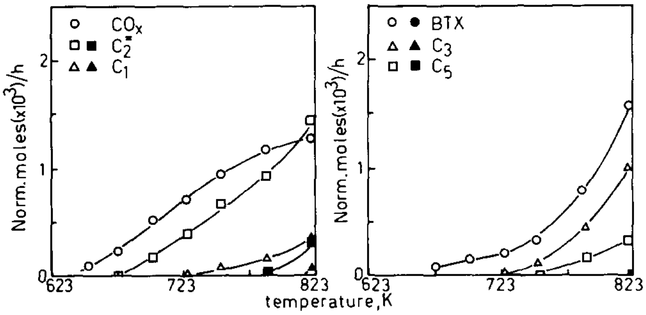

FIG. 5. Effect of reaction temperature on the normalized product distribution in ethane conversion on H-ZSM-5 (Si/Al = 164). Oxygen concentration 0.0% (solid symbols), 10.4% (open symbols).

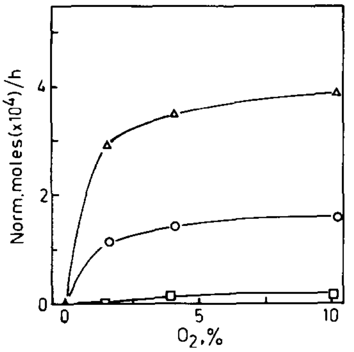

FIG. 6. Effect of oxygen concentration in the inlet reactant mixture on the normalized formation of aromatics from ethane at 753 K on H-ZSM-5 (Si/Al = 164). (□) Benzene, (△) toluene, (○) xylenes.

ZSM-5 at lower reaction temperatures. These authors also report the principal formation of C_7–C_8 aromatics from the C_2 hydrocarbon.

The effect of reaction temperature on the normalized product distribution in *n*-butane conversion is reported in Fig. 7 in both the presence and the absence of gaseous oxygen in the inlet reactant mixture. The activity of the zeolite in the C_4 conversion is much higher than the behavior in the conversion of lower alkanes. Under aerobic conditions the amounts of methane, C_2, and C_3 hydrocarbons formed increase only slightly, whereas a more significant effect is seen on the formation of aromatics. In the case of *n*-butane, C_9 aromatics also are detected together with BTX. The normalized formation of carbon oxides from *n*-butane (aerobic conditions) is approximately analogous to that of propane, whereas in the case of ethane a slightly higher total oxidation activity was observed.

The effect of the oxygen concentration on the formation of BTX aromatics from *n*-butane is shown in Fig. 8. In contrast to that found for ethane and propane, the aromatization activity depends on the oxygen concentration in the 0–10% range. Principal aromatics are toluene and xylenes with lower yields of benzene, in agreement with that found by other authors (*1*).

DISCUSSION

Role of Acid Sites in the Oxidation Activity

The acid–base properties of zeolites have been extensively characterized in the literature and the correlation with catalytic activity in hydrocarbon transformation is well known. However, the correlation between the presence of acid sites and the activity in the presence of gaseous oxygen is not so clear. The data in Figs. 1 and 2 and Table 1 clearly indicate the relationship between total oxidation activity (carbon oxide formation) and surface acidity. The normalized amount of CO_x is sufficiently independent from the nature of the hydrocarbon, but strongly dependent on the Si/Al ratio and the number of acid centers. The total oxidation activity falls to very low values when

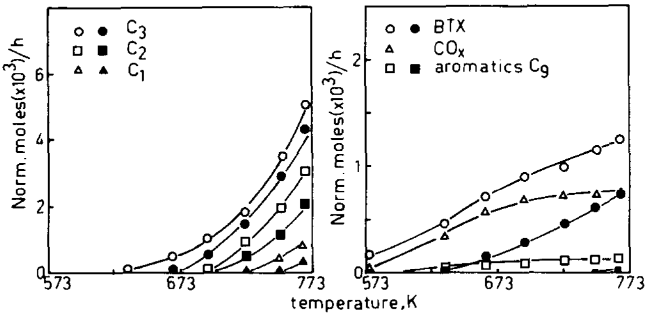

FIG. 7. Effect of reaction temperature on the normalized product distribution in *n*-butane conversion on H-ZSM-5 (Si/Al = 164). Oxygen concentration 0.0% (solid symbols), 10.4% (open symbols).

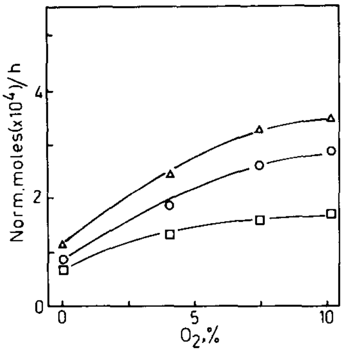

FIG. 8. Effect of oxygen concentration in the inlet reactant mixture on the normalized formation of aromatics from *n*-butane at 673 K on H-ZSM-5 (Si/Al = 164). (□) Benzene, (△) toluene, (○) xylenes.

surface acidity is inhibited by potassium exchange. These observations agree with the suggestion that the formation of carbon oxides may be ascribed to the reaction of the gaseous oxygen with the activated molecules formed in the interaction of the hydrocarbons with the acid centers of the zeolite. However, this effect suggests also that it is not possible under aerobic conditions to decrease the formation of carbon oxides without affecting at the same time the aromatization activity, since the same types of active sites are involved.

The second effect observed in the comparison of the aerobic behavior of the two H zeolites and of K zeolite is the dependence on the acid properties of propylene formation from propane. The effect is complex. This reaction depends to a much lesser extent on the number of acid sites than the total oxidation activity, as shown in Table 1 and in the comparison between the two zeolites with different Si/Al ratio. Therefore, the formation of olefins in the presence of O_2 depends on some specific characteristic of the zeolite, but the Brønsted acid sites are also involved in the mechanism. Dwyer (*30*) has recently discussed the mechanisms of hydrocarbon transformation on zeolites, concluding that the concepts of Brønsted and Lewis acidity are not sufficient to explain the catalysis over zeolites. Radical processes are well established on nonacidic zeolites (*31*) and a role for acid sites in generation or stabilization of radical species was suggested (*32*). On the other hand, we observe a specific effect in the presence of even low amounts of gaseous oxygen. The activity of free oxygen radicals in the activation of C–H bonds in light paraffins is well known and documented (*14*, *33*, *34*). O_2^- and O^- or other non-ESR-active adsorbed oxygen species may form olefins from paraffins at temperatures comparable to that of our tests. In addition, triplet oxygen is a stable free π-radical and at the temperature used in this study could be acting in this form. Oxygen-radical species may form on mixed oxides by the interaction of gaseous oxygen with surface-trapped electrons. In a recent work using ESR spectroscopy Shih (*35*) observed the presence of localized electrons (F centers) in ZSM-5 in the temperature range of our interest. These solid-state paramagnetic defects act as very energetic free radicals plausibly able to active oxygen forming oxygen free radical species. It is known that after zeolites have been γ-irradiated *in vacuo*, defect centers (F- and V-type) were produced which reacted with oxygen to form O_2^- species (*14*).

The nature of the solid-state defects present during reaction and able to activate oxygen, however, cannot be clearly established. Shih (*35*) suggests an oxygen role in the creation of these localized free electrons through a mechanism in which two Brønsted acid sites interact with oxygen forming solid-state defects. Present data are not fully in line with this hypothesis. We also noted a correlation between number of Brønsted sites and oxidative dehydrogenation activity. However, the sample with Si/Al = 164 and a very low Brønsted site density can hardly be activated by oxygen according to Shih's hypothesis. In contrast, the relatively high activity of this sample compared with ZSM-5 with Si/Al = 35 shows that the active sites in the aerobic conversion of alkane are not only generated according to Shih's mechanism (*35*). Strained T–O–T links are also proposed as sources of electron acceptor sites (*32*). It is likely that the number of these centers depends on the particular method of preparation used and may be different for the two zeolites examined. This can explain the nonlinear relationship between the aerobic activity and the Si/Al ratio. It should also be noted that Brønsted sites may be involved in the stabilization of radicals and radical ions generated by the interaction of alkane with electron acceptor sites. This interpretation may also explain the observed effect of Brønsted acidity on aerobic activity, in contrast to Shih's hypothesis.

Oxygen Effect in the Alkane Aromatization Mechanism

The catalytic aromatization behavior of unmodified H–ZSM-5 zeolites is usually related to their acidic properties as well as shape-selectivity effects. Thus the presence of gaseous oxygen is not expected to induce a possible modification in the formation of aromatics. However, in all cases, when the nature of either the H–ZSM-5 zeolite or the alkane was changed, an increase in the low-temperature aromatization activity of the ZSM-5 zeolites was observed. The effect is present for all alkanes and ZSM-5 zeolites tested and seems therefore to represent a more general aspect of the catalytic properties of these zeolites. The presence of oxygen in the gas phase mainly affects the formation of aromatics and olefins from the alkanes, but does not substantially change the nature of the products compared to anaerobic conditions.

In the Introduction we mentioned a possible oxygen effect in limiting deactivation coking. However, this seems not to be applicable to our case for the following reasons, at least below 773–823 K:

(i) Tests in a thermobalance, in agreement with literature data, indicate that the coke removal by oxygen starts at temperatures higher than around 773 K.

(ii) Figure 4 shows that the initial activity of the zeolite in the presence of oxygen is the highest one and that the rate of deactivation is higher under aerobic conditions than under anaerobic conditions.

(iii) The enhanced aromatization effect is prevalent at the lower reaction temperatures.

All these considerations therefore indicate a specific effect of the oxygen in the mechanism of aromatics formation.

Table 1 provides interesting information on this aspect and in particular suggests that the main oxygen effect is in the first stage of alkane activation, i.e., an enhancement of olefin formation. Higher activities of the olefins than of paraffins can then well explain the observed enhanced aromatization activity at the lower temperatures. In agreement, we noted that the second oxygen effect is the enhanced olefin formation compared with the anaerobic conditions (we operated at high space velocity in order to observe better the oxygen effects on the formation of all reaction products/intermediates). Accordingly, the enhancing effect is more drastic for the less reactive alkane (ethane) and for the less active ZSM-5 (Si/Al = 164). Also, this observation suggests a main oxygen effect in the stage of alkane activation, confirmed by the tests with the K zeolite. As previously discussed, localized surface defects formed in the oxygen interaction with Brønsted acid sites act as the active centers for the alkane activation and dehydrogenation to olefin whose higher reactivity explains the increased rate of BTX formation in the presence of oxygen.

Some other observations support this interpretation, as follows.

(i) In contrast to the behavior regarding carbon oxide formation, the aromatization activity drastically increases in the presence of even low amounts of oxygen. However, upon further increases in the oxygen concentration the rate of increase in aromatization activity slows considerably (Figs. 3 and 6).

(ii) The aromatization activity deactivates at a higher rate in the presence of gaseous oxygen than under anaerobic conditions (Fig. 4). This may be explained by the higher rate of aromatic formation. The coke can act as blocking active sites for oxygen activation. However, it should also be noted that due to the graphitic nature of the deactivating coke deposits, the aged catalyst is not nearly as good as fresh catalyst at producing free radicals (*35*), because the electrons are delocalized in the aged catalyst. The presence of carbonaceous materials thus also inhibits the formation of localized energetic radical species and, as a consequence, their activity in light alkane activation.

All these observations therefore suggest a possible role of free radicals in the first stages of BTX formation on H–ZSM-5. A number of recent communications (*36–38*) proposed that a free radical process based on the methoxy methyl radical is the dominant reaction pathway in methanol conversion. Other authors (*27, 39*) provide evidence against the involvement of radical intermediates in other stages of the reactions of dimethyl ether and methanol on H–ZSM-5, in particular in the deactivation mechanism. We may remark that our observations also are in favor of a possible role of free radical species in the first stages of the aromatization mechanism, especially at the lower reaction temperatures. However, it also should be noted that these centers seem to be present only in a very limited number, and especially that the formation of carbonaceous residues strongly inhibits this activity. This is in agreement with the results of Hunter *et al.* (*27, 39*) indicating a rapid deactivation with O_2 cofeeding during methanol and dimethyl ether conversion over H–ZSM-5. All these observations suggest that free radical pathways in the conversion of methanol to aromatics, although possible, may be of secondary importance, whereas their presence in the conversion of the much less reactive alkane may be more critical. It may finally be suggested that a modification of the zeolites or the addition of gas-phase co-reactants to enhance the formation of free radical species may represent a successful approach for the aromatization of light alkanes at low reaction temperatures, contrary to what is observed for methanol transformation (*27, 39*).

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