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Cumene Cracking on Dodecatungstosilicic Acid Catalyst

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Cumene cracking on supported $H_4SiW_{12}O_{40}$ was studied in the temperature range 150–244°C using a constant flow microreactor. In the initial periods of runs, besides the two predominant products benzene and propylene some less important amounts of C_4, C_5, and C_6 hydrocarbons as well as toluene and ethylbenzene were obtained. Based on these results and separate experiments with propylene and benzene, a reaction pattern was proposed. The side products vanished after some 10–20 min of run time during which there was rapid deactivation of the catalyst and a decrease from an initially high conversion to 20–30% conversion depending on temperature. From the mass balance the amount of carbonaceous deposit was estimated and it was shown that the precursors for its formation are propylene and cumene. Arrhenius plots of the rate constants at a given coking degree indicate that below 170°C at low coking degree it is the surface reaction which is the rate controlling factor. Above this temperature the reaction is predominantly a diffusion controlled process. © 1997 Academic Press

INTRODUCTION

Heteropoly acids (HPA), especially those with the Keggin type of anion structure, are known as catalysts for acid-catalyzed reactions (1). The Keggin units (KU) form a strongly hydrated secondary structure. Protons present in this secondary structure show strong acidity (2, 3) comparable with that of superacids (4). Due to these properties HPAs are active catalysts in such reactions as the dehydration of alcohols, e.g., ethanol (5, 6), 2-propanol (7, 8), butanol (9), and methanol conversion (10, 11). All of these mentioned reactions involve the HPA bulk and for this reason are called bulk type reactions (1, 12). HPAs are also catalysts in reactions of a different type, the so-called surface type reactions, in which reactants do not penetrate the bulk of the HPA crystallites and where it is mainly surface active centres which contribute to the catalytic process. Butene isomerization proceeds in accordance with this latter model (12).

Cumene cracking, a typical reaction occurring on the acid centres, was frequently investigated on zeolites (13, 14). The reaction kinetics as well as the mechanism of cumene cracking were studied by Corma and Wojciechowski (13) who proposed a detailed mechanism for this reaction. The deactivation of zeolite catalysts in cumene cracking was investigated by Dadyburjor *et al.* (15, 16). These authors proposed pore choking or active site suppression, depending on the coke level, as the reason for the deactivation of zeolite catalysts in cumene cracking (17).

Cumene cracking on heteropolyacids has been studied only rarely. To the knowledge of the present author, until now only two papers were published dealing with cumene cracking on heteropolyacids (7, 18). In both of them cumene cracking was used only as a test reaction in a pulse microreactor. Nowińska *et al.* (18) studied the effect of different catalyst supports at 150–320°C using $H_3PW_{12}O_{40}$ supported on MgO, γ-Al_2O_3, and silica. In (7), the yield of this reaction, as determined at 250°C, was used in order to compare the HPA activity in different catalytic reactions. No observations concerning the selectivity and side reactions, the effect of temperature, or the deactivation of the heteropolyacid catalysts was given.

The aim of the present research was to study the cumene cracking reaction in a more detailed way on a heteropolyacid catalyst. The initial experiments indicated that the high activity of the heteropolyacid is accompanied by deactivation and some changes in the selectivity. This paper deals with the catalytic behavior of unsupported dodecatungstosilicic acid ($H_4SiW_{12}O_{40}$, abbreviated as SiW).

EXPERIMENTAL

Preparation and Characterization of the Catalyst

Dodecatungstosilicic acid (Fluka, p.a.) was kept before the catalytic experiments under conditions of constant humidity. Differential thermal analysis (DTA) then showed full hydration with a content of 24 molecules of water of crystallization per KU. The preparation of the SiW samples for catalytic tests was carried out in a microreactor. The preparation required careful dehydration in a helium flow for 2 h at 40 to 60°C to avoid dissolution of the sample in its own water of crystallization (19, 20). DTA analysis of $H_4SiW_{12}O_{40}$ showed that the samples standardized according to this procedure were dehydrated but not

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dehydroxylated. The BET specific surface area of the dehydrated $H_4SiW_{12}O_{40}$ was 8 m^2 g^{-1}. Scanning electron microscopy (SEM) inspection of such dehydrated samples showed that the original crystallites of the order of 50 μm in size became aggregates of much smaller blocks (5 μm or less) separated by cracks and pores with widths of the order of 0.2 μm or less.

Reaction Procedures

The catalytic experiments were carried out in a continuous flow system, working under atmospheric pressure, connected on line with a gas chromatograph (GC). The microreactor was a quartz tube ($\phi = 10$ mm) with a thermocouple placed inside. Helium saturated with water vapour was used as the carrier gas (flow rate 30 ml/min). A fresh 0.2 g sample of pure SiW was taken for each run and pretreated just before the test. Subsequently the temperature was adjusted to the required value in the range 150–250°C and the catalytic test was started. Water vapour was introduced along with the helium to protect the catalyst against dehydroxylation during the catalytic run. Moreover, the presence of water facilitates the penetration of non-polar molecules into the HPA bulk (21). Cumene molecules have a dipole moment of $\mu = 0.65$ D (23); nevertheless, it was observed in a preliminary study that the presence of water vapour resulted in an improvement in the reproducibility of catalytic experiments. The carrier gas was saturated with cumene (Fluka, p.a.) at 20°C (constant concentration was 0.2 mol% cumene in helium). The amount of reactant was measured by GC analysis before and after passage of the reactant through the microreactor containing the catalyst. For the entire series of these experiments the contact time was constant and equal to 0.157 s and the weight hourly space velocity (WHSV) value was 0.122 h^{-1}.

Additional catalytic experiments were carried out with propylene and benzene instead of cumene. In the case of benzene, helium as the carrier gas was saturated with benzene (Fluka, pa) at 8°C (benzene concentration was equal to 2.2 mol% in helium). The tests with benzene were carried out at 240°C. In the tests with propylene the mixture of propylene (Fluka, p.a.) and helium (2.1 mol% of propylene in helium) was passed through the catalyst bed under atmospheric pressure. Tests were carried at 240°C with the same contact time, $\tau = 0.157$ sec; however, the WHSV $(g/g \cdot h) = 0.34$ was higher.

Analysis of Reaction Products

A Hewlett–Packard Gas Chromatograph 5890 Ser IIA connected on line was used for analysis of the reaction products. The separation of all reaction products formed under the described experimental conditions was achieved in a 2.4-m column filled with Chromosorb W acid washed with 9.9 wt% of silicone oil DC 200. Since the longest retention times of the observed products was less than 7 min, the catalytic runs were followed by analyses made every 7 min. A thermal conductivity detector (TCD) was used.

RESULTS

The major products of cumene cracking on pure solid $H_4SiW_{12}O_{40}$ (SiW) were propylene and benzene. Some side products were observed in the first few minutes of the run. They were hydrocarbons C_4, C_5, C_6, toluene, and ethylbenzene. The isomers of these hydrocarbons were seen in the chromatographic analysis but were not separated. The side products vanished after 10–25 min run time. This period of time became shorter at higher temperatures.

The catalytic results were expressed using the following parameters:

α_k, total cumene conversion (total catalytic activity), (expressed in %mol); amount of moles of cumene consumed divided by the amount of moles of cumene introduced;

α_c, conversion in cumene cracking (%mol); amount of moles of cumene cracked to benzene divided by the amount of moles of cumene introduced, a parameter equal to the molar yield of benzene;

y_i, molar yield of a particular product i (%mol); amount of moles of product i divided by moles amount of cumene introduced;

m_a, mass of accumulated deposit (mg); accumulated loss of mass of introduced cumene per 0.2 g SiW of catalyst during the catalytic run.

The fresh samples showed very high activity. Depending on temperature the initial conversion was 80–100 mol%. It decreased during the catalytic run, indicating strong deactivation of the sample. The activity stabilized at a level of 20–30% after 30–40 min of run time. Figure 1 shows the typical behaviour of the SiW catalyst during the runs at temperatures 158–237°C.

Figure 2 shows the yield of benzene and propylene as a function of run time. The yield of benzene changed with time in parallel with the conversion of cumene represented in Fig. 1, whereas the yield of the second main product,

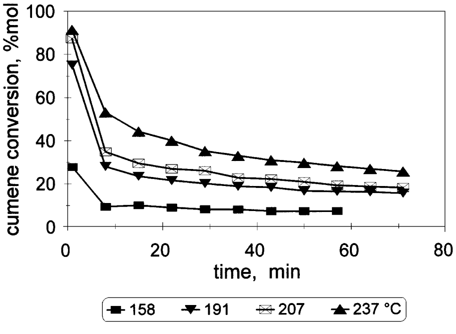


FIG. 1. Total conversion of cumene versus reaction time.

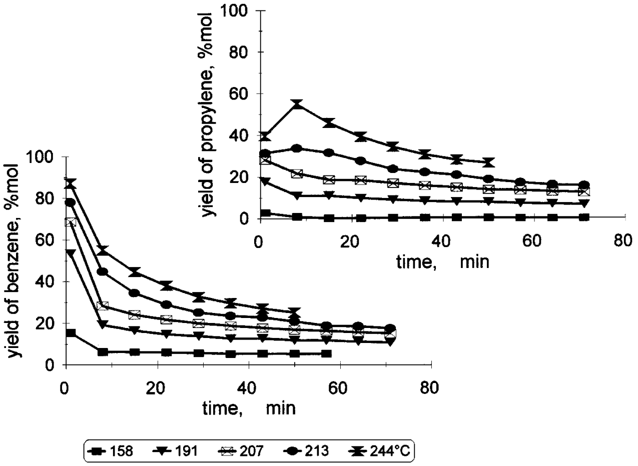


FIG. 2. Molar yield of benzene and propylene versus time.

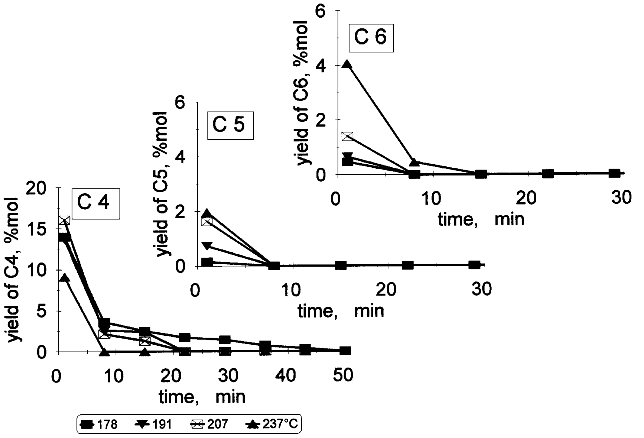


FIG. 4. Molar yields of C_4, C_5, and C_6 hydrocarbons versus time.

propylene, at high enough temperatures (≥213°C) passed over a local maximum after about 10 min. Figure 2 also shows that at lower temperatures the molar yield of propylene was definitely lower than that of benzene, thus indicating strong deviation from the stoichiometric molar ratio of propylene/benzene equal to one in the cracking of cumene. This is better represented by Fig. 3 where the propylene/benzene molar ratio is plotted against run time carried out at different temperatures. It is seen that even on the fresh catalyst the stoichiometric ratio was never reached and there was a very distinct deficit of propylene in respect to benzene. The propylene/benzene ratio reached a practically constant value after some 10–15 min at all investigated temperatures. At 170°C it was as low as about 0.3 but was close to unity at about 240°C.

Figures 4 and 5 show the molar yield of the side products, namely C_4, C_5, and C_6 hydrocarbons (some isomers of these hydrocarbons were observed but were not chromatographically separated), toluene, and ethylbenzene. It is seen that the rate of their formation is highest on the surface of the fresh catalyst at the very beginning of the run. However, it decreases rapidly with reaction time. C_4 hydrocarbon formation was the only side reaction observed for a time as long as 50 min or so, especially at rather low temperatures. The longer-chain hydrocarbons C_5 and C_6 appeared in smaller amounts (the yield of C_5 was twice as low as that of C_6) and vanished after about 10–15 min.

Toluene in appreciable amounts was observed only on the fresh samples, whereas ethylbenzene, similarly to C_4, was detected for a much longer period of time, up to about 40 min at the lowest temperature.

The quantitative comparison of cumene conversion and the amounts of all products observed in the gas phase indicate a significant mass deficit. On the fresh sample the mass deficit ranged up to ~25 wt% of introduced cumene and diminished during the run, reaching a practically constant level of ~5–10 wt%, depending on the temperature (higher level at lower temperatures).

This mass deficit is evidently due to the formation of some kind of carbonaceous residue on the catalyst.

For the sake of comparison, additional test on a SiW sample (pretreated according to the standard procedure) was carried out with propylene as the reactant at 240°C. The conditions of this experiment were similar to those in the case of cumene. C_4, C_5, and C_6 hydrocarbons were observed as gaseous reaction products. Some isomers of

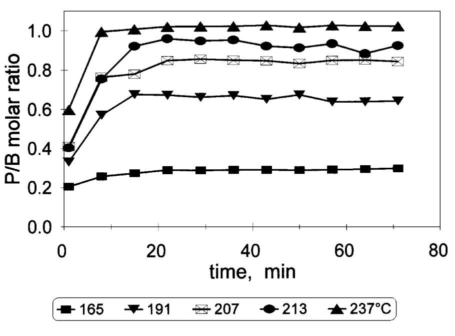


FIG. 3. Propylene/benzene molar ratio versus time.

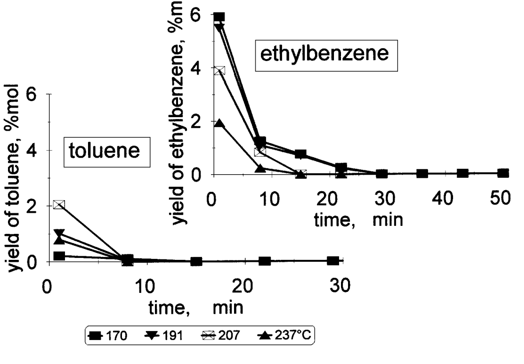


FIG. 5. Molar yields of toluene and ethylbenzene versus time.

these hydrocarbons were observed but were not separated. The amounts of the particular hydrocarbons observed were in the order $C_4 > C_6 > C_5$. No aromatics were formed in the propylene conversion on the SiW catalyst.

Propylene conversion, calculated from the difference between the amounts of propylene detected in the gas phase before and after introduction to the catalyst, which was initially as high as about 6 mol%, decreased rapidly and after about 30 min reached an almost constant level of ∼1.5 mol%. At the same time, the total yield of products observed in the gas phase did not exceed 4 mol% for the fresh sample. The mass balance indicated that some amount of introduced propylene always remained on the catalyst, assumedly forming the carbonaceous deposit. This mass deficit decreased from a value of about 2 mol% at the beginning of the test to 0.5 mol% after 30 min. The yield of C_5 hydrocarbons observed as the product of propylene conversion decreased quickly to traces only. However, C_4 and C_6 hydrocarbons were observed in measurable quantities until the end of the test.

A similar experiment was carried out with benzene as the reactant at 240°C. The fresh SiW sample was pretreated as described. No products of catalytic activity were seen during the entire run and only negligible amounts (of the order 0.1 mol%) of benzene were lost, thus showing that benzene was not transforming nor forming carbonaceous residue on the catalyst.

DISCUSSION

The results show that $H_4SiW_{12}O_{40}$ is an active catalyst for the cumene cracking reaction. However, its activity rapidly decreases with reaction time. As already stated, depending on the temperature, the initial cumene conversion of 75–100 mol% diminishes over the course of 10–15 min to an almost constant level equal to about 20 mol% at 170°C and 30 mol% at 244°C. Besides the main products, benzene and propylene, the products of secondary reactions, C_4, C_5, and C_6 hydrocarbons, ethylbenzene, and toluene, also appear in the initial period.

The high activity of the heteropolyacids in cumene conversion (reaching 80–90 mol%) was also found by Nowińska *et al.* (18) in the case of catalysis by dodecatungstophosphoric acid ($H_3PW_{12}O_{40}$). Considering the fact that $H_4SiW_{12}O_{40}$ is a very strong protonic acid (the value of the Hammett acidity function of the less-acid $H_3PW_{12}O_{40}$ was estimated to be of the order $H_0 \leq -13.16$ (4)) and that cumene cracking is believed to need protonic acid centres with strength $H_0 \leq -5.6$ (18), we conclude that the main reaction

$$C_6H_5 \cdot C_3H_7 \rightarrow C_6H_6 + C_3H_6 \qquad [1]$$

occurs on the Brønsted acid centres. It also seems justified to accept that the observed side reactions need the most strongly acid centres which are gradually blocked during the initial period of the catalytic run. The poisoning of the strongest acid sites may be the reason for the rapid decrease of the side product yields.

As Fig. 3 shows, only at the highest temperatures investigated is the propylene/benzene molar ratio close to the stoichiometric value 1. At temperatures below about 240°C it decreases and at 170°C it is as low as about 0.3. These facts find an easy explanation in our observation, after the tests with benzene as the reactant, that benzene is not adsorbed on the solid $H_4SiW_{12}O_{40}$ under the catalytic reaction conditions and that appreciable amounts of propylene may be bonded to the catalyst surface. It is logical to ascribe this latter fact to the presence of the carbocation $C_3H_7^+$ which may subsequently initiate the formation of a propylene oligomer:

$$xC_3H_6 \rightarrow \text{oligomer}. \qquad [2]$$

During the additional catalytic test with pure propylene some amounts of C_4, C_5, and C_6 hydrocarbons were observed as the reaction products, which also appear as the minor products of cumene cracking. These facts lead to the conclusion that all three of the hydrocarbons mentioned above are the products of a transformation of the primary propylene produced in the course of cumene of cracking. Neither ethylbenzene nor toluene were formed during the tests with propylene, thus indicating that these compounds are not the result of propylene conversion but rather are formed in other side reactions of cumene.

The behavior of the fresh catalyst can be best presented by discussing the results obtained after 1 min of run time. The initial yields of C_4, C_5, and C_6 presented in Fig. 6 as a function of reaction temperature show a very strong predominance of C_4 with a maximum at about 215°C.

The maxima of C_5 and C_6 yields at about 250°C may be interpreted as the result of accelerated decomposition of propylene oligomer (it will be shown later that in this temperature region the amount of oligomer distinctly decreases). The oligomers observed by Datka (22) on HY zeolites decomposed with a preferential C_4 hydrocarbon formation. Nevertheless, in the case of SiW the domination of C_4 at lower temperatures can be only partially due to

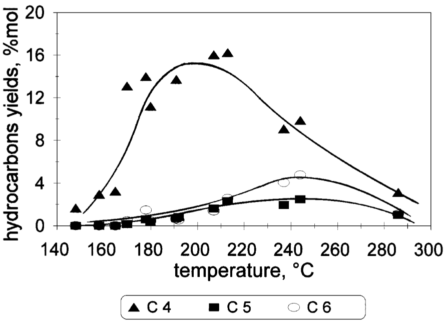


FIG. 6. Molar yields of C_4, C_5, and C_6 hydrocarbons after 1 min of reaction time versus reaction temperature.

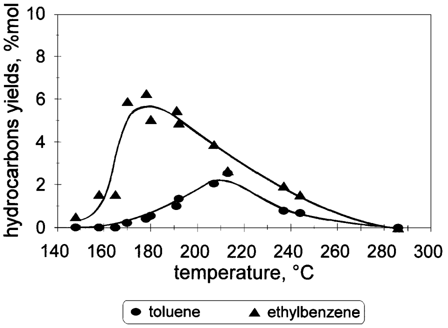


FIG. 7. Molar yields of toluene and ethylbenzene after 1 min of reaction time versus reaction temperature.

the oligomer decomposition and some other sources of this hydrocarbon must be proposed.

The mechanism of cumene cracking on heteropolyacids was not investigated nor discussed in the literature; for this reason the results obtained in the present study will be discussed in comparison with the mechanism of cumene cracking on zeolites proposed by Corma and Wojciechowski (13). These authors proposed a mechanism of ethylbenzene formation based on the reaction:

$$2\, C_6H_5 \cdot C_3H_7 \rightarrow C_6H_6 + C_6H_5 \cdot C_2H_5 + C_4H_8 \qquad [3]$$

The conclusion that on the SiW catalyst ethylbenzene and C_4 are produced in reaction [3] is strongly supported by the fact that the yields of both products are changing in a parallel way with temperature changes, as can be seen by comparing Figs. 6 and 7. Nevertheless, according to Corma and Wojciechowski, reaction [3] needs both Lewis and Brønsted acid centres (both present in zeolites). The presence of the Brønsted centres on SiW is obvious but not the Lewis acid centres. In this situation the abstraction of a hydride ion H^- from the cumene molecule by strongly acid protons supplied by Brønsted acid sites is conceivable. However, in this case molecular hydrogen should be formed in the products and this was not observed. It is also conceivable that such H_2 molecules "*in statu nascendi*" are consumed in hydrogenation reactions, e.g., as hydrogenation of the carbonaceous residue. It should be mentioned here that in the case of the $H_4SiW_{12}O_{40}$ catalyst no cymene, *n*-propylbenzene, or ethyltoluene was observed, which according to Corma and Wojciechowski are forming on Lewis acid sites present in zeolites.

In the present study a certain amount of toluene appeared at the beginning of the run. It may be the product of the reaction:

$$2\, C_6H_5 \cdot C_3H_7 \rightarrow C_6H_5 \cdot C_2H_5 + C_6H_5 \cdot CH_3 + C_3H_6. \quad [4]$$

The initial toluene yield, which was very small at lower temperatures, reached an appreciable value (~2 mol%) at about 200°C while the other product of reaction [4], namely ethylbenzene, exhibited a much higher yield within the whole range of temperatures. When comparing Figs. 6 and 7 we can suggest that on a SiW catalyst below 215°C ethylbenzene forms mainly according to reaction [3], but above this temperature reaction [4] predominates.

Let us now discuss in a more detailed way the formation of the carbonaceous residue. It should first be recalled that a molar ratio of propylene and benzene close to one, as expected from the stoichiometry of Eq. [1], was found only at the highest temperature, and in most cases was distinctly below this value (Fig. 3). The deficit of propylene with respect to benzene is evidently due to its oligomerization and the formation of a carbonaceous deposit after the partial decomposition of the oligomer. However, the mass deficit was always appreciably higher than the amount of deficient propylene. There was also a further calculation of the mass deficit where the contribution of cumene was calculated from the balance of aromatic rings and the contribution of propylene was calculated from the balance of all carbon atoms. Reactions [1], [3], and [4] have to be taken into account, and the results of these calculations over the entire run time are shown in Fig. 8. The data points in Fig. 8 display the instantaneous mass deficit found in each particular gas chromatographic analysis.

It should be remembered that in a separate experiment it was proved that benzene does not accumulate on the catalyst. Hence these calculations indicate that cumene also participates in the formation of the deposit. This does not necessarily mean that two separate types of deposits are present but does indicate the simultaneous contribution of propylene and cumene in the formation of the deposit on SiW.

An example of the effect of temperature on the magnitude of both components in the deposit formation after 8 min of run time is shown in Fig. 9. The amounts of both are highest at about 170°C but the cumene contribution in the carbonaceous residue dominates in all of the investigated temperature range. At the highest temperatures the propylene contribution in the deposit is practically negligible. This

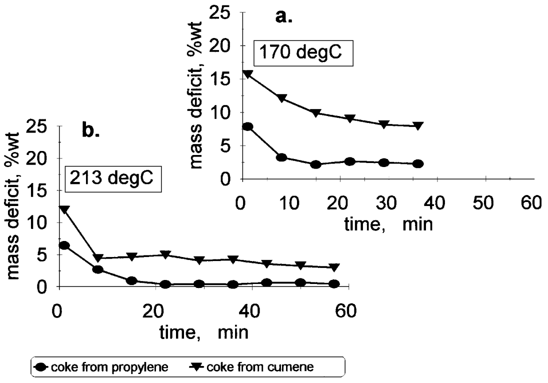


FIG. 8. Participation of cumene and propylene in the formation of deposit as the function of time at (a) 170°C and (b) 213°C.

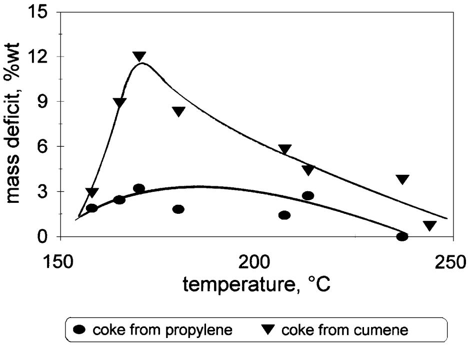


FIG. 9. Participation of cumene and propylene in the formation of deposit as a function of temperature at 8 min of reaction time.

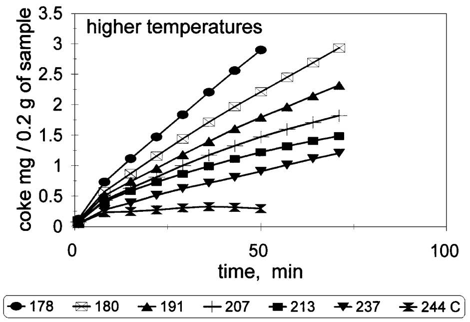
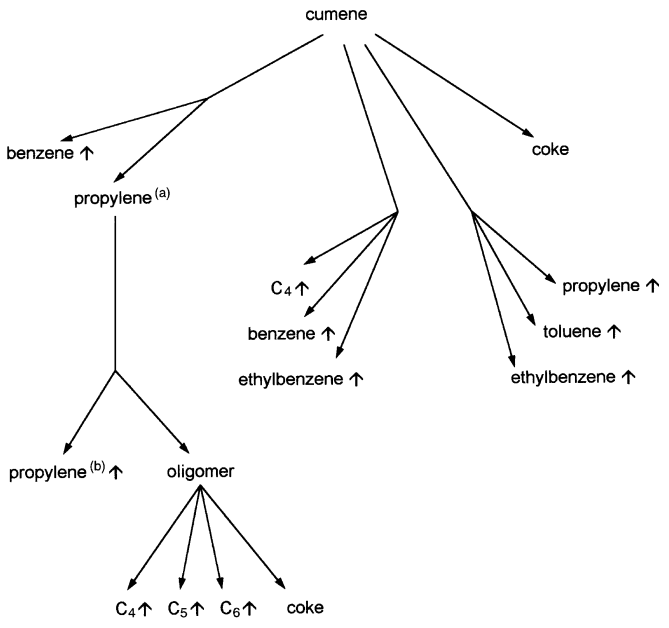


FIG. 10. Accumulated coke amounts formed in the higher temperature range (i.e., above 170°C) versus time.

is understandable when one takes into account, as was explained above, that the propylene contribution to the deposit formation passes via oligomer decomposition and that the oligomer creation at temperatures as high as 240°C is suppressed (22).

The above discussion of the catalytic behaviour of the $H_4SiW_{12}O_{40}$ catalyst enables the scheme of cumene conversion on dodecatungstosilicic acid illustrated in Scheme 1 to be proposed.

Mass deficits found from particular chromatographic analyses allowed calculation of the total accumulated amount of deficit (without differentiation on propylene or cumene contributions) deposited on SiW samples during the run. This was done by integration of curves such as those shown in Fig. 8 in the time intervals 0–*t* and adding the values of both integrals. The accumulated amount of deposit increases when the temperature is raised from 148 to 170°C and decreases on raising the temperature any further. Figure 10 shows the accumulated deposit value (m_a) for the higher temperature range.



(a) - propylene formed in cumene cracking

(b) - propylene evolved into the gas phase

SCHEME 1

As Dadyburjor *et al.* (15, 17) have pointed out, the presence of coke affects the catalytic behaviour of zeolites in cumene conversion. The coking may influence the rate of the catalytic reaction either by site suppression, which is the result of adsorption of coke molecules on catalytically active centres, and/or by choking the pores present in the catalyst, e.g., in its volume or in the coke layer. The first factor is expected to play the predominant role in the initial period of the catalytic process when the individual coke molecule may be sufficient to tie up the single active site. This offers a reasonable explanation of the rapid initial deactivation (observed also in our case on SiW). On the other hand, the slow deactivation observed in the latter stages of the catalytic process may be due rather to the increased diffusional resistance in the catalyst. Discrimination between the two factors was proposed by Dadyburjor (15) to be possible by considering a series of Arrhenius plots where each of them corresponded to a different but constant coke amount on the catalyst. According to this model each constant coke Arrhenius plot consists of two intersecting linear parts. The changes of slope in the low and high temperature ranges depends on the character of the deactivation process.

Dadyburjor *et al.* (15) discussed in his paper two limiting cases. In the first one only site suppression is taken into account as the reason for catalyst deactivation, and in the second only pore choking is responsible for the deactivation process. In the first case the activation energy in the low temperature region decreases with increasing coking but is constant in the high temperature region. This means that the slopes of the low temperature sections of the Arrhenius plots are different for different m_i values, whereas slopes in the high temperature range remain parallel. In this case only site suppression is responsible for the deactivation.

In the second limiting case, according to Dadyburjor there is no change of low temperature activation energy (all of the slopes of the constant coke Arrhenius plots in the low temperature range are parallel) but the high temperature activation energy decreases with increasing coking, i.e., there is increasing pore choking.

In our case, for the SiW catalyst we approximated the curves of m_a shown in Fig. 10 using a power function which made it possible to interpolate the time t_i after which a given amount of the deposit (coke) m_i was reached (the values of m_i 0.5, 0.75, 1.0, etc., in mg/0.2 g of catalyst were chosen).

The curves of the cumene cracking conversion α_c (equal to the molar benzene yield) as a function of time were also approximated using a power function which enabled calculation of the conversion $\alpha_c(m_i)$ corresponding to the particular values of m_i. Assuming first order kinetics of the cumene cracking, the values of the rate constants k_i at a given coke level m_i were calculated. Using these values, constant coke Arrhenius plots were obtained. They are shown in Fig. 11.

It can be seen that the plots are composed to two linear sections which intersect at points corresponding to a temperature of about 170°C. The apparent activation energies calculated from the slopes of low and high temperature sections are given in Table 1.

It is seen from Fig. 11 and Table 1 that at each coke level the slopes changed both in the low and the high temperature regions. This means that on the $H_4SiW_{12}O_{40}$ catalyst both effects (site suppression and pore choking) are present. At temperatures below 170°C the apparent activation energy is the highest at the lowest coke level, $m_i = 0.5$ mg/0.2 g of catalyst. The highest apparent activation energy may be considered as the activation energy corresponding to the almost fresh catalyst. However, it decreases slowly with increasing coking and for the $m_i = 3$ mg/sample it reaches about two-thirds of the initial value, thus indicating that an appreciable portion of the very active sites was eliminated.

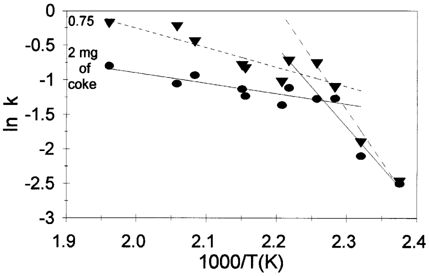


FIG. 11. Cumene conversion to benzene. Arrhenius plots at different amounts of accumulated coke (expressed in mg of coke/0.2 g of catalyst).

TABLE 1

Apparent Activation Energies of Cumene Conversion to Benzene

Amount of accumulated coke/0.2 g catalyst (mg)	Apparent activation energies (kJ/mol)	
	Temp. range below 170°C	Temp. range above 170°C
0.5	122.0	19.2
0.75	123.4	23.4
1	115.4	18.8
1.25	108.7	17.5
1.5	102.3	15.5
1.75	99.5	13.8
2	95.8	12.5
2.5	89.5	10.0
3	84.5	8.4

A very low activation energy within the high temperature region is typical of a diffusion controlled reaction. The data in Table 1 show that a transition to the diffusion controlled reaction was observed under the present conditions of catalytic testing also at the lowest coking degree, which suggests that in this temperature region reaction in the pristine catalyst also occurs partially on the internal surface of pores present in the highly porous catalyst sample. The penetration of molecules of cumene exhibiting a dipole moment $\mu = 0.65$ D (23) into the bulk of HPA crystallites cannot be excluded.

With increasing coking the apparent high temperature activation energy further decreases. Presumably this is the situation when coking results in a complete closing of a certain amount of pores.

CONCLUSIONS

It has been shown that solid dodecatungstosilicic acid exhibits high activity in the catalytic cracking of cumene. Besides the formation of benzene and propylene as the main products, several side reactions occur resulting in the formation of ethylbenzene, toluene, and C_4, C_5, and C_6 hydrocarbons, and also in the oligomerization of propylene. A reaction scheme for cumene conversion on $H_4SiW_{12}O_{40}$ was proposed based on the observed yields of particular products. Gradual deactivation of the catalyst was observed which was attributed to the formation of the carbonaceous residue. The amount of deposit was estimated on the basis of the mass balance, which indicates that both propylene and cumene participate in the formation of the carbonaceous residue. Following the suggestion of Dadyburjor, constant coke Arrhenius plots were obtained which enabled us to draw the conclusion that in the case of catalysis by dodecatungstosilicic acid, deactivation was due to both the poisoning of the active centres and the blocking of the diffusion channels in the highly porous catalyst.

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