

Catalysis by Coke Deposits: Synthesis of Isoprene over Solid Catalysts

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The formation of coke deposits on solid catalysts is a problem of great concern for many catalytic processes, since it leads to catalyst deactivation. Nevertheless, in some catalytic applications it can play a positive role in the generation of highly efficient active sites and in the formation of active “working” catalysts.^[1] The concept of catalysis by carbonaceous deposits was formulated more than 40 years ago.^[2] According to this concept, the catalytically active surface of a catalyst is formed during coke deposition, and the active sites of the “working” catalyst are quite different from those of the fresh catalyst and involve reactive carbonaceous species, such as surface carbenium ions or radicals. Among the catalytic reactions which obey this concept are such well-known industrial processes as “methanol to olefins” (MTO),^[1a-c] the skeletal isomerization of *n*-butenes,^[1d] the hydroisomerization of long-chain *n*-alkanes,^[1e] and the alkylation of toluene^[1f] and naphthalene.^[1g] These processes were the subject of a comprehensive review by Guisnet.^[3] A general feature of all these processes is the existence of the induction period, during which the active surface species are formed. The identification of such species, unraveling of the mechanism of the induction period, and the elucidation of the chemical process that takes place after the induction period are the main steps required for the understanding of catalyst deactivation.

Herein, we report on the key role of carbonaceous deposits in the synthesis of isoprene from formaldehyde and isobutene over solid catalysts. Today, isoprene is mainly produced by extraction from the C₅ fraction of naphtha steam cracking, and therefore its output is entirely dependent on ethylene production. However, ethylene producers are switching to more efficient technologies for ethylene production. This trend will lead to a lack of isoprene on the market; thus, alternative technologies are required for its synthesis. The condensation of formaldehyde with isobutene is among the most attractive alternative technologies for the synthesis of isoprene.

The main industrial process based on this route involves two steps: 1) the liquid-phase condensation of isobutene with formaldehyde under the catalysis of aqueous sulfuric acid and

2) the vapor-phase decomposition of 4,4-dimethyl-1,3-dioxane (DMD) to isoprene over solid phosphoric acid catalysts.^[4] This process has many drawbacks involving economical, technological, and environmental issues, such as low efficiency and selectivity, corrosion, and separation problems. Therefore, the future challenge in this area is the development of a one-step selective process based on solid catalysts.

The solid catalysts studied so far in the condensation of isobutene with formaldehyde include zeolites,^[5] oxides,^[6] sulfates,^[7] phosphates,^[8] and heteropolyacids.^[9] Although some of these catalytic systems showed rather high initial yields of isoprene (60–70 %) in the direct synthesis,^[5-9] they exhibited rather low selectivity and very short life times owing due to rapid deactivation because of fast coke formation. Analysis of the results indicates that for the most active catalysts, there is usually an induction period before the activity reaches the steady state.^[6-9]

These observations brought us to the hypothesis that carbonaceous deposits formed during the induction period may play an important role in the one-step synthesis of isoprene. In this study, we aimed to clarify the nature of carbonaceous deposits formed during the induction period and their role in the mechanism of condensation of formaldehyde with isobutene over niobium oxide, which is among the most active and selective catalysts for the Prins condensation.^[6c]

To prepare the active niobium oxide catalyst with a high surface area and high acidity, we subjected a commercial Nb₂O₅ sample to redispersion and hydration by a dissolution–precipitation procedure described by Ushikubo et al.^[10] The catalyst obtained had a surface area of 70 m² g⁻¹ and an acid-sites content of 240 μmol g⁻¹, as determined by measurement of the temperature-programmed desorption of ammonia.

The conversion of isobutene and formaldehyde over hydrated niobium oxide was studied in a continuous flow reactor at 573 K in the presence of excess isobutene (C₄H₈/CH₂O 7:1; a more detailed description of the preparation and characterization of the catalyst and experimental techniques is given in the Supporting Information). The yields of the main reaction products are plotted versus time on stream (TOS) in Figure 1.

The formation of isoprene is preceded by an induction period. During this period, the main reaction products are carbon monoxide, hydrogen, and methylbutenes (MBs). Carbon monoxide and hydrogen are formed by the decomposition of formaldehyde over Nb^{δ+}–O^{δ-} ion pairs.^[8b,11] The rapid decrease in the yield of carbon monoxide with TOS can be explained either by surface hydration and the transformation of Lewis acid sites into Brønsted acid sites, which are responsible for condensation reactions,^[8b] or by rapid poisoning of the active sites by carbonaceous deposits.

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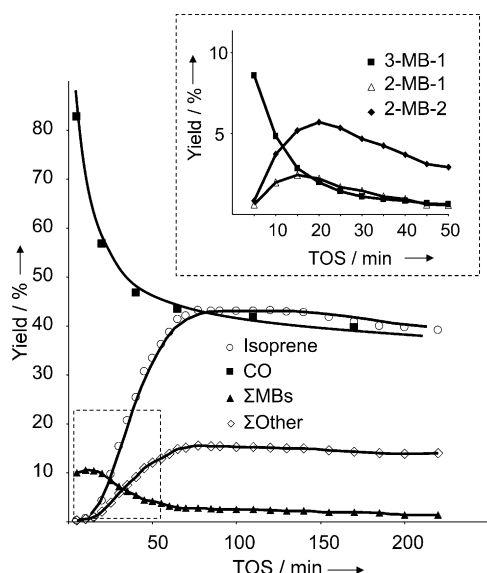


Figure 1. Yield of products plotted versus TOS for the reaction of formaldehyde with isobutene over hydrated Nb_2O_5 (isobutene/formaldehyde 7:1, weight hourly space velocity (WHSV): $3.8 \text{ g g}^{-1} \text{ h}^{-1}$, $T = 573 \text{ K}$). 3-MB-1 = 3-methyl-1-butene, 2-MB-1 = 2-methyl-1-butene, 2-MB-2 = 2-methyl-2-butene.

The main by-products observed during the steady-state period were 2,2,4-trimethylpentenes, methylcyclopentadiene, 4,4-dimethyl-1,3-dioxane, 2-methylbutanal, 4-methyldehydropyranes, and 3,4,4-trimethylcyclohexene. 2,2,4-Trimethylpentenes are formed by the oligomerization of isobutene, whereas all other compounds are products of formaldehyde and isobutene condensation followed by isomerization, cyclization, and dehydration reactions. The main reaction pathways leading to these products have been described elsewhere.^[8b]

To elucidate the reasons for the induction period in isoprene formation, we investigated the accumulation of carbonaceous deposits over the niobium oxide catalyst. For this purpose, the catalytic experiments were interrupted after various periods of time, and the coke accumulated on the catalyst was analyzed by the thermogravimetric (TG) technique. We found that the carbonaceous deposits were mostly formed during the induction period (Figure 2). This result indicates the key role of coke in the selective synthesis of isoprene. The nature of coke also changed during the induction period:

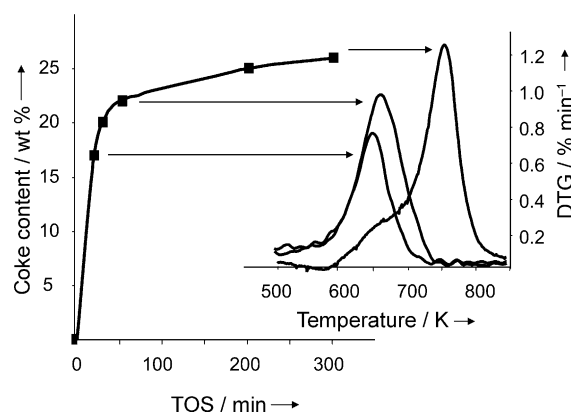


Figure 2. Variation in the coke content of the Nb_2O_5 catalyst with TOS and DTG curves obtained after 20, 50, and 300 min on stream.

the differential thermogravimetric (DTG) peaks shifted towards higher temperatures, which points to the transformation of soft coke into hard coke.^[12]

More detailed information on the nature of coke accumulated during various periods of the reaction was obtained by treating the used catalysts with CH_2Cl_2 and analyzing the extracted carbonaceous deposits by GC-MS (Figure 3).^[13] In the early stages of the reaction (20 min on stream), the carbonaceous deposits contained mainly ethers, esters, and acetals with a chain length of 3–7 carbon atoms and substituted cyclopentenones and cyclohexenones containing 7–9 carbon atoms. At longer reaction times (50 min on stream), the ester and ketone content decreased drastically, whereas ethers were still present. Finally, at the steady state

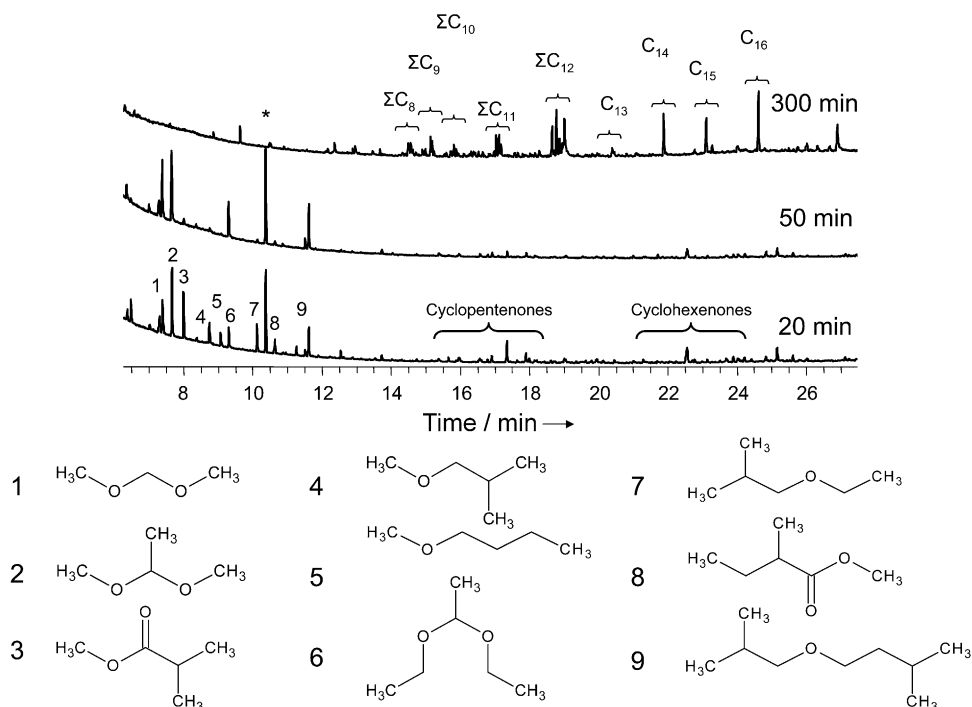


Figure 3. GC-MS analysis of coke deposits accumulated on Nb_2O_5 after 20, 50, and 300 min on stream. The C_8 – C_{16} compounds indicated in the top spectrum are olefin and polyene species. The signal marked with an asterisk is due to a contaminant in the solvent.

(300 min on stream), the carbonaceous deposits were mostly long-chain alkenes containing 8–16 carbon atoms.

The ^1H - ^{13}C cross-polarization magic-angle spinning (CPMAS) NMR spectrum obtained for the catalyst after 300 min on stream confirms the GC–MS results on the nature of the carbonaceous deposits (Figure 4a). The peaks at $\delta = 30.2$ and 20.3 ppm can be attributed to saturated carbon

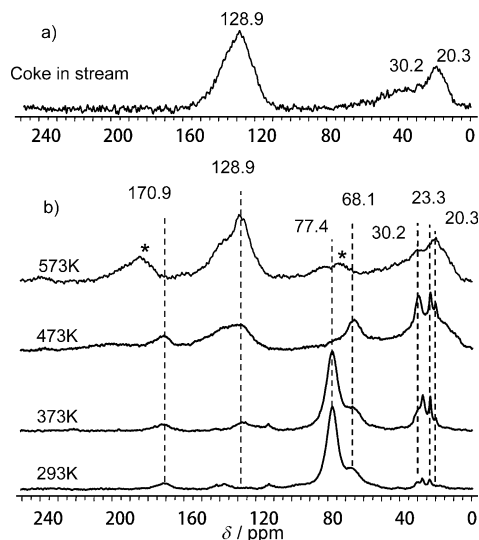


Figure 4. ^1H - ^{13}C CPMAS NMR spectra obtained for the Nb_2O_5 catalyst a) after 300 min on stream in a continuous flow reactor and b) during the course of in situ experiments at various reaction temperatures. Signals marked with asterisks are due to side bands.

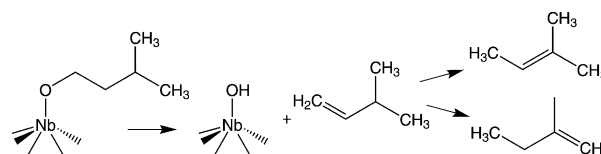
atoms of branched aliphatic compounds, whereas the intense broad peak at $\delta = 128.9$ ppm is due to olefinic carbon atoms.^[14,15] Thus, all the results obtained suggest that on the fresh catalyst surface, oxygen-containing carbonaceous deposits are formed, whereas at longer reaction times these compounds are converted into branched polyenic coke, which is most probably responsible for selective isoprene formation at longer times on stream.

To gain deeper insight into the mechanism of active-coke formation, we studied the initial stages of the reaction by in situ ^1H - ^{13}C CPMAS NMR spectroscopy (Figure 4b). [^{13}C]H $_2$ O was used as the labeled reactant. The first major peaks observed at $\delta \approx 77.4$ and 68.1 ppm after the coadsorption of [^{13}C]H $_2$ O and unlabeled isobutene can be assigned to surface alkoxides and ethers.^[15] The peaks observed are different from those detected previously during the interaction of formaldehyde^[16] or isobutene^[17] individually with acidic catalysts, which suggests that they arise from the interaction of both reactants with the catalyst surface. The observation of surface alkoxides and ethers during the initial steps of the in situ experiments is in line with the results of the GC–MS analysis of coke deposits formed during the induction period in a continuous flow reactor (Figure 3).

An increase in the reaction temperature led to the disappearance of the signals at $\delta \approx 77.4$ ppm and then at $\delta \approx 68.1$ ppm and the appearance of peaks in the spectral regions of $\delta = 20$ –30 and 120–140 ppm corresponding to

saturated and unsaturated carbon atoms of branched olefins and polyenic species.^[15,18] Thus, the initially formed surface alkoxides and ethers are decomposed into alkenes, which undergo further reactions that lead to long-chain oligomeric carbonaceous deposits.

The decomposition of surface alkoxides at the early stages of the reaction may account for the formation of 3-methyl-1-butene (Scheme 1), which was observed as the only primary

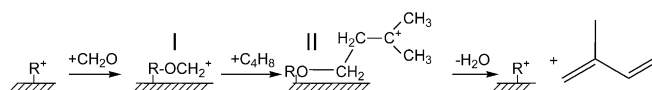


Scheme 1. Mechanism of early stages of surface reactions.

product during the induction period in the experiments in a continuous flow reactor. 3-Methyl-1-butene can undergo isomerization to 2-methyl-1-butene and 2-methyl-2-butene (Scheme 1) and oligomerize to give long-chain olefins, as confirmed by the analysis of reaction products (Figure 1) and carbonaceous deposits at longer reaction times (Figures 3 and 4).

Finally, heating to 573 K resulted in complete transformation of the reactants into olefinic coke, which was very similar to that observed in the experiments in the continuous flow reactor (Figure 4a,b). This coke is composed of C_8 – C_{16} branched unsaturated hydrocarbons, which are most probably protonated at the acidic sites of niobium oxide and can initiate the reaction of formaldehyde and isobutene to enable selective isoprene formation.

The results obtained can be further rationalized by the reaction pathway in Scheme 2. In the first step, the interaction of formaldehyde with the carbenium ion of active coke leads



Scheme 2. Proposed reaction pathway for the formation of isoprene.

to carbocation I, which further interacts with isobutene to form carbocation II. Further decomposition of carbocation II yields isoprene and water and results in restoration of the active site.

In conclusion, the key role of unsaturated branched carbonaceous deposits in the synthesis of isoprene over solid catalysts has been demonstrated. The mechanistic pathway involves the accumulation of unsaturated branched surface species during the induction period, followed by their interaction with formaldehyde and isobutene through an addition–cleavage mechanism to promote selective isoprene formation. The mechanism proposed shows the way forward for further catalyst improvement. In particular, the analysis of

coke deposits obtained on different acidic catalysts will enable the relationship between the type of active coke formed and the selectivity of the catalyst to be established. This information will provide a key to the design of an efficient solid catalyst for the synthesis of isoprene.

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