JOURNAL OF CATALYSIS 145, 295–299 (1994)

Surface Carbonaceous Deposits as Activity and Selectivity Influencing Species in Ring-Opening Reactions of Propylcyclobutane Catalyzed by Pt/SiO_2

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Received March 8, 1993; revised July 14, 1993

Active site formation in the hydrogenative ring opening of propylcyclobutane over Pt/SiO_2 was investigated in a static reactor, mainly at 373 K. Changes in the ring-opening rates and selectivities on variously treated catalyst are described. Three types of treatment were applied: repeated runs with (i) only evacuation or (ii) inter-run reduction (H_2, 473 K, 0.5 h), or (iii) prepoisoning of the catalyst with propylcyclobutane at 373 K or 673 K. The observed (in some cases dramatic) increase in selectivity towards the formation of heptane (1,2 C-C bond scission) is interpreted in terms of the formation of a metal-carbonaceous deposit interface where the deposit provides an anchoring site for the adsorption of the propyl side-chain and the ring opens on the clean Pt atoms. Changes in activity due to the various treatments are also discussed. © 1994 Academic Press, Inc.

INTRODUCTION

The fast build-up of surface hydrocarbon coverage is a quite general phenomenon in catalytic hydrocarbon transformations on platinum and other transition metals. The structure of the reactant, the reaction time and temperature, and the hydrogen partial pressure are the main variables determining the nature of such surface carbonaceous species. Their structure can be drastically altered by further treatments.

The formation, composition, and reactivity of surface hydrocarbon deposits in skeletal rearrangements and alkene hydrogenation have been intensively studied in recent years, for reviews, see, e.g., (1–3). Important results on single crystals have emerged from Somorjai's laboratory (4). Their main findings regarding the transformations of saturated hydrocarbons indicate that the carbonaceous deposit acts as a nonselective poison which blocks the platinum surface sites, thereby preventing the adsorption of reactant molecules. It also plays an important role in supplying hydrogen to reacting surface species and providing desorption sites for product molecules.

Eminent observations are also available on polycrystalline catalysts. Gravimetric measurements relating to hexane on Pt black revealed the presence of two fundamental types of adsorbed species. The reversibly held fraction regarded as the reactive surface intermediate in hydrocarbon transformations can be hydrogenated off the surface. The proportion of irreversibly bound, hydrogen-poor species increases considerably with elevation of the reaction temperature, or on heat treatment in vacuum or inert atmosphere (5). Evacuation without concomitant heat treatment also transforms hydrogen-rich, reversibly held carbonaceous residues to more firmly held, hydrogen-poor species (6). Independent studies involving a number of other methods on Pt/Al_2O_3 have provided notable additional information on the location and structure of coke deposits (7, 8).

These observations indicate that nongraphitized carbonaceous residues take part in the surface reaction in one way or another; i.e., they are part of the active center.

Other, quite different views of the role of carbonaceous overlayers in catalytic systems must also be mentioned. Beebe and Yates (9) and Cogen and Maier (10) found complete insensitivity to carbonaceous build-up in the hydrogenation of ethylene on Pd/Al_2O_3 and in H/D exchange on Rh black. In their opinion, the carbonaceous surface species are only bystanders in these reactions and they are not part of the active center. Burwell and coworkers recently arrived at the same conclusions (11).

It must be emphasized, however, that in spite of the controversies around the precise role of carbonaceous species, their existence on working metal catalysts or single crystals is not debated.

We earlier reported that the high initial rates in the hydrogenative ring opening of propylcyclobutane on Pt/SiO_2 decreased in time, lower, steady-state activities being attained (12). The product accumulation versus re-

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0021-9517/94 $5.00

action time curves could be separated into two linear parts: the steeper first part corresponding to a higher initial activity, and the second part, with a lower slope, representing a less active state. This phenomenon became more pronounced with increasing temperature. These observations, which suggested the apparent formation and involvement of carbonaceous deposits in ring opening, prompted the present study. Our aim was to acquire more information and a better understanding of the formation and stability of the carbonaceous species possibly involved in the hydrogenative ring opening of cyclobutanes on platinum.

EXPERIMENTAL

Propylcyclobutane (100% pure by GC) was subjected to several freeze–thaw–evacuate cycles before use. Oxygen-free hydrogen was prepared with a Matheson 8326 generator, operating with a palladium membrane. The 3% Pt on Cab-O-Sil (Cab-O-Sil M5 silica, product of BDH, BET surface area 241.6 m^2 g^{-1}) catalyst used was prepared by impregnating the support with H_2PtCl_6 solution. The air-dried catalyst precursor was prereduced at 773 K for 16 h under flowing H_2. The dispersion of the catalyst as determined by hydrogen chemisorption and electron microscopy was 11.8% and 11.5%, respectively. For more details, see (12, 13).

Measurements were carried out in a conventional closed recirculation reactor. The catalyst sample (10 mg) was activated in 26.6 kPa hydrogen at 473 K for 0.5 h. The system was evacuated, and was heated or cooled to the reaction temperature. After admission of a mixture of 1.33 kPa propylcyclobutane and 20 kPa hydrogen to the reactor, the system was filled with Ar to atmospheric pressure, and product yield vs time functions were determined. A Carlo Erba Fractovap 2150 gas chromatograph (FID detector, 4-*m* 5% bis(methoxyethyl)adipate or 3.6-*m* 20% squalane on Chromosorb PAW columns) was used for product analysis. For more details, see (12–14).

Five types of experiment were carried out. In restart reactions, the transformation of propylcyclobutane under identical conditions (373 K, 50 min reaction time) on the same catalyst sample with fresh reaction mixture in each experiment was repeated 8 times, with evacuation of the reactor after each reaction cycle (10^{-3} Pa residual pressure, 15 min). In a second set of experiments, every reaction sequence was followed by activation of the catalyst in 26.6 kPa hydrogen for 30 min at 473 K. The third type of measurements involved rate and selectivity studies over catalyst samples deliberately precovered with a hydrocarbon overlayer. In these reactions, the catalyst was kept in 1.33 kPa propylcyclobutane without hydrogen for 30 min at 373 K or 673 K. After evacuation, reactions were run at the above temperatures under standard conditions.

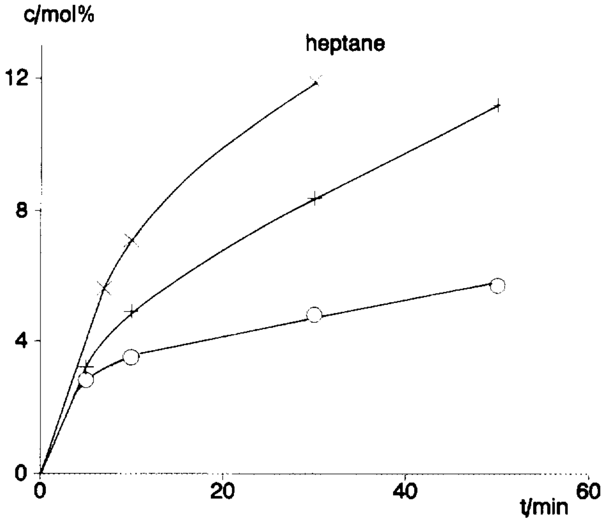

FIG. 1. Examples of product yield vs time functions for heptane formation in restart experiments at 373 K. Runs: (×) 1, fresh, (+) 2, run 3; (O) 3, run 7.

In the fourth type of experiments 30 mg of catalyst was used. A propylcyclobutane—hydrogen mixture in the same ratio as in kinetic measurements (2.67 kPa propylcyclobutane and 40 kPa hydrogen) was allowed to react at either 373 K or 673 K for 1 h. Then the reactor was evacuated to 10^{-1} Pa (to avoid further dehydrogenation of surface species due to high vacuum, but to remove the reaction mixture from the gas phase), and 20 kPa H_2 was introduced into the system. It was reacted over the used catalyst at 423, 573, and 673 K for 1 h at each temperature. The desorbed products were analyzed. Finally, intentional coking was done with 2.6 kPa propylcyclobutane at 673 K for 0.5 h. Then 20 kPa H_2 was used in attempting to hydrogenate residues off the surface as in the fourth set of experiments.

Blank experiments revealed that there was no homogeneous reaction even at 673 K, and the support was also inactive. Moreover, the unreduced catalyst was inactive as well.

RESULTS

Restart Reactions

Restart reactions are expected to provide information about the continuous build-up of the carbonaceous layer during repeated runs of the ring-opening reaction under identical conditions. Important features of this study are as follows:

(i) As pointed out previously (12), initial and steady-state activities in the product accumulation versus reaction time functions could hardly be distinguished at 373 K reaction temperature (Fig. 1, curve 1). On repetition

TABLE 1

Activity (molecules exp. atom^{-1} s^{-1} × 10^{-2}) and Selectivity Data for the Ring Opening of Propylcyclobutane in Restart Experiments

Run	Initial overall rate	Steady-state overall rate	$r_{heptane}/r_{overall}$	
			Initial	Steady-state
1	10.4	3.1	0.7	0.6
2	8.3	3.6	0.7	0.6
3	6.8	2.2	0.7	0.6
4	12.7	4.1	0.7	0.6
5	9.8	3.9	0.7	0.6
6	10.8	3.0	0.7	0.6
7	5.7	0.9	0.8	0.5
8	5.0	0.6	0.8	0.6

of the reaction on the same catalyst sample with fresh reaction mixtures, the difference becomes more and more pronounced (Fig. 1, curves 2 and 3). This indicates that the quantity of surface residues formed on an initially clean platinum surface in a single reaction run under the given reaction conditions (low temperature) is too small to affect the rate of the ring-opening transformations.

(ii) Ring-opening rates in restart reaction sequences, though somewhat scattered, do not change much up to the sixth run. Significant deactivation occurs in the last two experiments, however (Table 1, columns 2 and 3).

(iii) We previously reported the unexpected selectivity of platinum in the ring opening of propylcyclobutane, yielding heptane as the major product through rupture of the sterically more hindered 1,2 C–C bond in preference to 3-methylhexane formed as a result of 2,3 C–C bond scission (12). In restart experiments, heptane is likewise the major initial product and it stays so over the working catalyst. The selectivity of heptane formation over the working surface practically does not change in this set of experiments (Table 1, column 5). Nevertheless, the initial selectivities are slightly shifted toward heptane formation after six consecutive runs (Table 1, column 4).

Effect of Reactivation in Hydrogen

The second set of experiments was performed by reactivating the catalyst sample after each run. The most important observations are as follows:

(i) The hydrogen-treated used catalyst exhibits significant activity increase in the initial stage of the reaction as well as in the steady-state region (Table 2, runs 1–3). This activity increase is further accentuated in run 4. On a fresh, initially clean catalyst sample no reaction could be observed at 323 K. In contrast, the reactivated catalyst exhibits a fair catalytic activity at this temperature.

(ii) An even more surprising change can be seen in the ring-opening selectivities. In run 4 at lower reaction temperature, both initially and on the working catalyst, the ring opens exclusively in the sterically more hindered direction.

(iii) Increasing reaction temperature results in a dramatic activity drop and diminishing selectivity on the reactivated sample (Table 2, run 5). This is not unexpected, though, since a rate decrease of almost the same magnitude occurs on a fresh catalyst (12). When used again at the original reaction temperature, the catalyst sample with this background exhibits only a very low activity (Table 2, run 6). Surprisingly, however, exclusively heptane is formed.

Catalytic Activity and Selectivity of Platinum Precovered with Carbonaceous Deposits

As compared with the initially clean platinum catalyst, samples deliberately precovered with carbonaceous deposit exhibit minor activity changes at 673 K reaction temperature. In contrast, marked activity drops occur at 373 K. The most striking feature again is the exclusive formation of heptane at this reaction temperature, no matter whether the poisoning of the catalyst was carried out at 373 or 673 K (Fig. 2a and b).

Carbonaceous Residues over Catalysts Treated under Various Conditions

To obtain direct evidence about the existence of carbonaceous species over the used or deliberately precovered catalysts and to gather qualitative information about their hydrogen content, the hydrogenative removal of the carbonaceous residue layer from the surface was attempted.

This can be done when a 1-h reaction with a propylcyclobutane–hydrogen mixture is performed at 373 K. Here, 3-methylhexane and heptane desorb at 423 K. Se-

TABLE 2

Activity (molecules exp. atom^{-1} s^{-1} × 10^{-2}) and Selectivity Data for the Ring Opening of Propylcyclobutane in Reactivation Experiments

Run	Reaction temp./K	Initial overall rate	Steady-state overall rate	$r_{heptane}/r_{overall}$	
				Initial	Steady-state
1	373	10.4	3.1	0.7	0.6
2	373	18.8	4.9	0.7	0.6
3	373	29.7	4.9	0.6	0.6
4	323	1.4	0.2	1.0	1.0
5	673	5.6	0.6	0.7	0.5
6	373	1.6	0.01	1.0	1.0

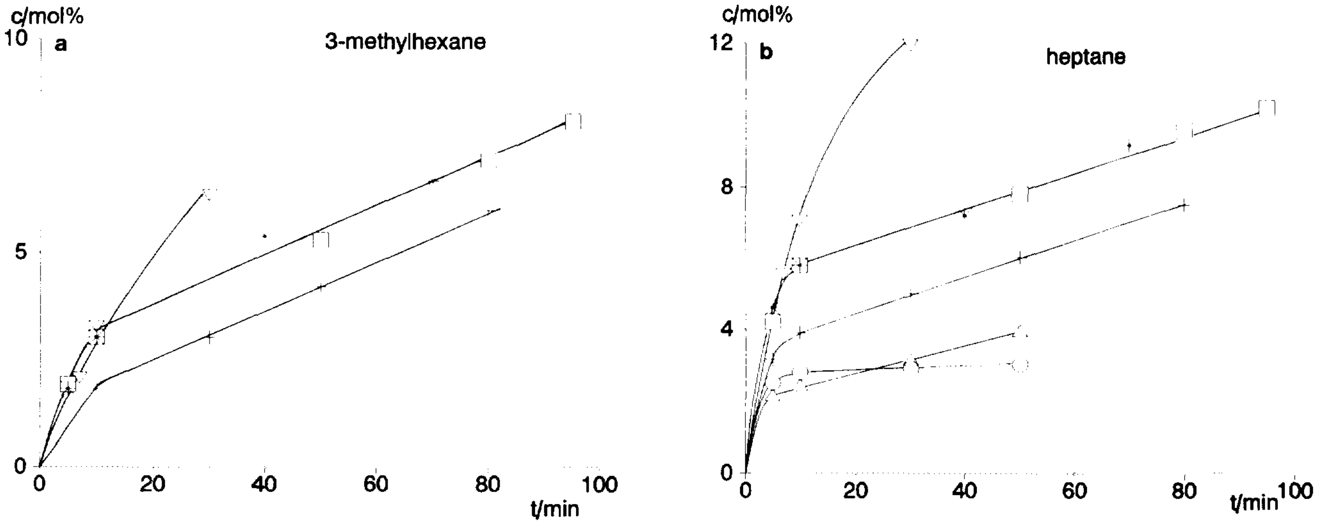

FIG. 2. Product yield vs time functions for the formation of (a) 3-methylhexane, (b) heptane in experiments (r.o. 373 K or r.o. 673 K are the temperatures of hydrogenative ring opening), where the catalysts were precovered with 1.33 kPa of propylcyclobutane at 373 K or 673 K (denoted c. 373 K or c. 673 K, respectively). (▽) Fresh 373 K; (*) fresh 673 K; (○) c. 373 K, r.o. 373 K; (□) c. 373 K, r.o. 673 K; (Δ) c. 673 K, r.o. 373 K; (+) c. 673 K, r.o. 673 K.

lectivity towards heptane is 0.8, just as in the 7th and 8th restart reactions. As the temperature is raised (no evacuation was done) the quantity of desorbed products decreases and they disappear at 673 K. When a similar mixture reacts at 673 K for 1 h the quantity of 3-methylhexane and heptane hydrogenated off the surface at 423 K decreases to 7.5% of that evolved in a similar treatment after a ring-opening reaction at 373 K. Heptane selectivity was 0.7, close to the steady-state selectivity of the reaction at 673 K (12). As the temperature is raised the desorbed products disappear again.

When propylcyclobutane alone reacts on the surface at 673 K for 0.5 h, nothing can be removed from the surface with hydrogen treatment.

DISCUSSION

Experimental results show that during the ring-opening reaction of propylcyclobutane several types of carbonaceous residue form. The hydrogen content of these carbonaceous species can be influenced significantly. Successive runs of heat treatment and/or prolonged evacuation without reduction in between (6) transform weakly held hydrogen-rich carbonaceous residues to a layer which is firmly attached to the surface and contains considerably less hydrogen. Actually, weakly held hydrogen-rich carbonaceous species formed at 373 K are surface intermediates of the reaction. In restart experiments they gradually lose hydrogen, slow down the ring-opening reaction, and to some extent influence ring-opening selectivity, i.e., pushing it towards heptane formation. The ring opens predominantly via 1,2 C–C bond scission at 373 K over the fresh catalyst (12), which is quite unusual, since it is well known that hydrogenative ring-opening reactions of substituted ring systems take place predominantly through the rupture of the sterically less hindered C–C bonds over platinum (and other transition metal) surfaces and this type of transformation requires free metal sites (1–3, 15, 16). Accordingly, studies on the transformation of methylcyclopentane on platinum single crystals (16) and supported platinum catalysts strongly indicate that ring opening in the less hindered direction (formation of 2-methyl- and 3-methylpentane) takes place on the clean metal surface (17). In contrast, hexane formation, i.e., ring scission in the more hindered direction, is proposed to occur on adlining sites of platinum and the support, i.e., at the metal–support interface (18). Our results also indicate an adlineation mechanism even over the fresh catalyst (12). During coke formation, the highly dehydrogenated species which start to form on metallic sites gradually spill over to the support (7): thus, the proportion of interfaces increases considerably, while that of the free metal sites diminishes. Consequently, the overall rate decreases, while selectivity towards heptane formation increases, sometimes dramatically. The deposit serves as an anchoring site for the propyl group, thereby facilitating the appropriate geometry for 1,2 C–C scission, i.e., for the preferential or exclusive formation of heptane. The actual ring opening takes place on metallic sites.

In reactivation experiments the ring-opening rate increases considerably, and selectivity towards heptane formation decreases. As independent studies indicate, this treatment causes rearrangement of this surface layer, bringing about the reappearance of larger ensembles of surface metal atoms (19). Since metallic sites favor the rupture of the sterically less hindered C–C bond, the relative weight of this transformation route should increase and indeed so does it.

CONCLUSION

The unusual regioselectivity, i.e., the predominant or the exclusive scission of the sterically hindered C–C bond in the hydrogenative ring opening of propylcyclobutane over the clean and the carbonaceous Pt/SiO_2, led us to conclude that the metal–support and metal–carbonaceous deposit interfaces play crucial role in the transformation. The support and/or the carbonaceous residues provide anchoring sites for the side-chain adsorption of propylcyclobutane, and the fixed geometry allows only or mainly the scission of the sterically more hindered C–C bond, which occurs over metallic sites. Therefore, we incline to the view that nongraphitic, though hydrogen-poor surface carbonaceous species and also the metal–support interface are part of the active center for this reaction.

ACKNOWLEDGMENT

We acknowledge the support provided for this research by the Hungarian National Science Foundation through Grants 1871/1991 and 1885/1991.

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