CARBON MOLECULAR SIEVE SUPPORTS FOR METAL CATALYSTS—II. SELECTIVE HYDROGENATION OF HYDROCARBONS OVER PLATINUM SUPPORTED ON POLYFURFURYL ALCOHOL CARBON

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Abstract—The system platinum supported on a carbon molecular sieve has been prepared by carbonizing polyfurfuryl alcohol containing chloroplatinic acid and an activated carbon filler. Static adsorption results indicated that this material could be roughly classed as a 5A molecular sieve since its capacity for butane was 6 times that for isobutane. In addition, evidence was obtained for the presence of slit-shaped pores or pore constrictions. Using a continuous flow technique, shape selectivity was demonstrated for the competitive hydrogenations of 3-methyl-1-butene with both 1-butene and cyclopentene. No such selectivity was observed in the 1-butene: isobutene system, probably due to the planar structure of isobutene and the significant diffusivity of isobutane at the reaction temperature used.

1. INTRODUCTION

The concept of using molecular sieves or molecular sieve-supported catalysts for performing shape selective chemical reactions was first thoroughly demonstrated by Weisz and co-workers[1–3] beginning in 1960. If the catalytically active surface can be made accessible to reactants only through pores of molecular dimensions, shape or size selective reactions may be performed. For example, a 5A zeolite containing active platinum was prepared which allowed 1-butene to be selectively hydrogenated in a reactant stream containing isobutene, which was unable to penetrate the essentially circular micropores of the zeolite due to its larger molecular size in one direction[2].

Walker and co-workers[4–6], as well as others[7–9], have prepared molecular sieves from various carbons. As carbons may offer some advantages over zeolites as catalyst supports in reactions where dual-functionality is not desired, it was thought that the preparation of a carbon molecular sieve (CMS)-supported catalyst should be investigated. Cooper and Trimm[10, 11] have recently described preparations of CMS-platinum catalysts and have performed several selective reactions using a pulse flow technique. Conversions were low, however, and catalyst deactivation rapid.

In this paper we describe shape selectivity obtained for several olefin hydrogenation reactions using a carbon molecular sieve-platinum system in a continuous flow reactor.

2. EXPERIMENTAL

Composite carbon molecular sieve (CCMS)-platinum catalysts were prepared by carbonizing polyfurfuryl alcohol(PFA) containing a measured amount of chloroplatinic acid

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solution and various proportions of activated carbon filler to produce the desired molecular sieve effect. Details of these preparative techniques are available elsewhere [12]. Briefly, the preparation of the system used in this study was as follows: Clear, freshly distilled PFA from the Quaker Oats Company was mixed with phosphoric acid solution and heated, with occasional stirring, to 90–95°C. The pH of the solution at this point was 1·5. Heating was continued for 3 hr after which a water solution of chloroplatinic acid, containing 0·05g Pt/cm^3 and partially neutralized with sodium hydroxide, was added along with the desired weight of 28 × 150 mesh activated carbon. The activated carbon was grade UU from Barnebey–Cheney Co., the weight ratio of PFA to carbon used was 5·0. After 1 hr of soaking at 90–95°C, the mixture was cured in N_2 for 4 hr at 110–150°C, followed by 14 hr at 190–220°C. The cured sample was carbonized in a flowing He stream by heating at 7°C/min to 700°C and soaking for 1 hr. The final sample contained 0·98% Pt by weight. A sized sample, 20 × 100 mesh, was used for the catalysis studies. Static adsorption, with 1 hr allowed for adsorption, gave 'monolayer equivalent' areas of 410, 180, and 30 m^2/g for CO_2 (−77°C), n-butane (0°C), and iso-butane (0°C), respectively.

Competitive hydrogenation of various pairs of olefins was studied with a Pyrex and Tygon flow system consisting of flowmeters, bubblers for entraining liquid hydrocarbons, and a U-tube immersed in a constant temperature bath. The catalyst was placed on a fritted glass disk in the downstream leg of the U. A plug of glass wool kept the catalyst in place as the reactant mixture was passed upward through the bed. The upstream leg of the tube served as a preheater. Hydrogen was passed through a deoxo unit, dried with Drierite, and used as a carrier. The hydrocarbons, generally 99·0% pure, were used as received. Analysis was by gas chromatography. Samples were withdrawn through serum caps, located both before and after the bed, by means of gas-tight syringes. A standard catalyst pre-treatment of 2 hr at 400°C in 50–100 cm^3/min hydrogen was found to give reproducible results.

A commercial 1% Pt/C catalyst (Engelhard Industries), showing no molecular sieve properties for the hydrocarbons involved, was used to obtain competitive reactivities for the various pairs of olefins employed. It had a butane surface area of 1170 m^2/g.

To begin the experiments, 1·21 g of CCMS–Pt catalyst were weighed into the 11 mm Pyrex reactor tube. This gave a bed height of 21 mm and a volume of 2·0 cm^3; the same sample was used for all the reactions described in this paper. The Engelhard catalyst was found to have a considerably higher activity than the CCMS–Pt catalyst for hydrogenation. Therefore, since we were concerned primarily with relative hydrogenation rates in this study, the amount of Engelhard catalyst used was reduced to 0·016 g of 28 × 150 mesh material. The bed volume in this case was 0·04 cm^3. Under these conditions, and by using a deficiency of hydrogen with the Engelhard catalyst, the rates of hydrogenation of those hydrocarbons, for which diffusion resistance was relatively small, were comparable.

3. RESULTS

The first reaction system studied was the 1-butene: isobutene: hydrogen system. Although the branched isobutene molecule might be expected to be unreacted over the CCMS–Pt catalyst, such was not the case, as Fig. 1 shows. In fact, results with the CCMS–Pt catalyst were in good agreement with those for the commercial Pt/C catalyst, which gave conversions of 20% for isobutene and 50% for 1-butene when the olefins were in equimolar amounts but reacted with insufficient hydrogen.

When 1-butene was reacted competitively with 3-methyl-1-butene, the results shown in Fig. 2 were obtained. This is a good
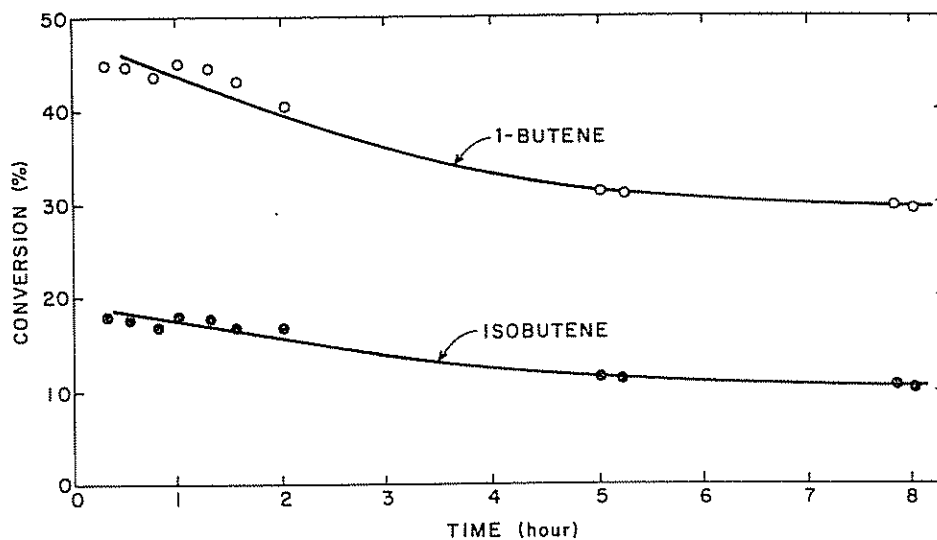
Fig. 1. Competitive hydrogenation of 1-butene (O) and isobutene (⊜) over CCMS–Pt catalyst. H_2: 1-C_4H_8: i-C_4H_8 equals 4:1:1. Residence time, 1·0 sec. Temperature, 160°C.
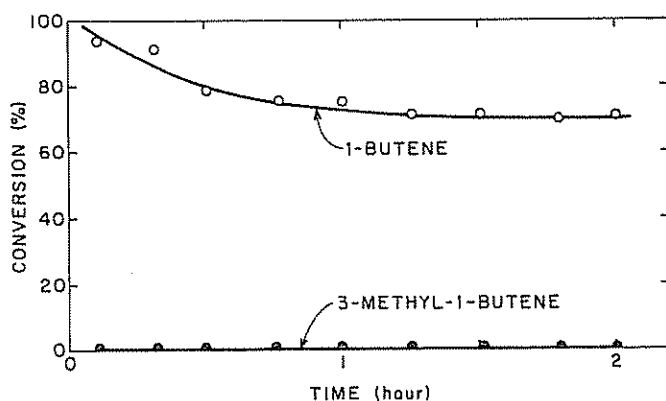

Fig. 2. Competitive hydrogenation of 1-butene (O) and 3-methyl-1-butene (⊜) over CCMS–Pt catalyst. H_2: 1-C_4H_8: 3-methyl-1-butene equals 40:4:1. Residence time, 1·8 sec. Temperature, 150°C.
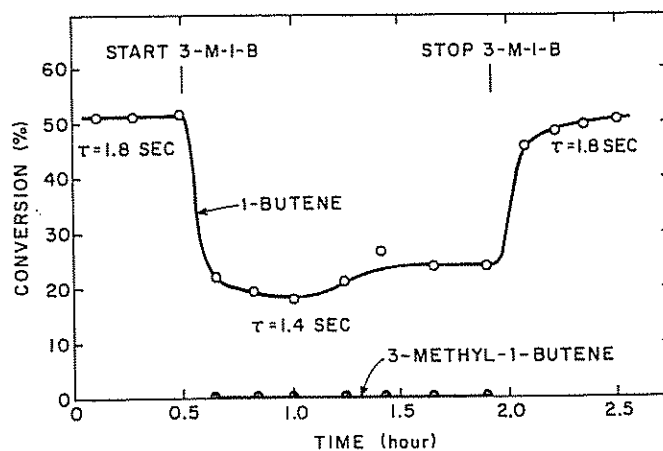

Fig. 3. Influence of 3-methyl-1-butene (⊜) on the hydrogenation of 1-butene (O) over CCMS–Pt catalyst at 82°C.

example of shape selective catalysis. When a similar reactant mixture (but deficient in hydrogen) was passed over the commercial catalyst and conditions adjusted to give 80–90% conversion of 1-butene to n-butane, about 50% of the 3-methyl-1-butene was converted to 2-methyl-butane. In addition, most of the remaining 3-methyl-1-butene was isomerized to 2-methyl-2-butene and 2-methyl-1-butene. No such isomerization was observed over the CCMS–Pt catalyst.

The addition of 3-methyl-1-butene to a 1-butene: hydrogen flow (Fig. 3) caused a decrease in 1-butene conversion, which may be attributed to the shorter residence time as well as to the dilution of the reactant stream. No hydrogenation of 3-methyl-1-butene was observed, and cessation of its addition was followed by a rapid increase in 1-butene conversion which approached its initial level.

Table 1 gives the results of an experiment in which 3-methyl-1-butene and cyclopentene were used as reactants. The data are average conversions obtained after essentially constant activity was reached; although conversions

Table 1. Competitive hydrogenation over CCMS–Pt and commercial Pt/C catalysts

Reactants	Conversion, %	
	CCMS–Pt*	Pt/C
cyclopentene	8	12
3-methyl-1-butene	2	20

*Temp = 150°C, residence time = 2·0 sec, H_2: total olefin = 4:1. Mole ratio of hydrocarbon reactants = 1 for each catalyst.

were small, the CCMS–Pt catalyst showed a clear preference for the hydrogenation of cyclopentene, reversing the result obtained with the commercial catalyst.

4. DISCUSSION

Unlike zeolites, most non-graphitizing carbons obtained by thermal degradation of polymers have no discernable crystal structure. Thus an exact determination of pore sizes is very difficult, particularly in the 5–15A range of interest in molecular sieve studies. Gas adsorption methods and, particularly, molecular probe techniques are most often used. Most of the difficulties involved in the study of microporous carbons are well illustrated by Bond[13]. One important property of such carbons is that they always contain a distribution of pore sizes, thus complete separation of molecules with closely similar dimensions is difficult to achieve.

A second important property of microporous carbons, with regard to molecular sieve effects, is the shape of the pores or pore constrictions. A number of investigations[4–6] have indicated the likelihood of such constrictions being slit-shaped. Thus, planar molecules, such as benzene, could often be preferentially adsorbed over cyclohexane. Isobutene is also a planar molecule and in fact was found to be adsorbed by the CCMS–Pt catalyst used in this study to an equal or greater extent than 1-butene. Thus the results shown in Fig. 1 are not

surprising. Apparently, at the temperature of the reaction, the isobutane formed within the pore system of the catalyst possessed sufficient kinetic energy to overcome the activation energy necessary to diffuse out of the pores without causing rapid catalyst deactivation. This is in spite of the fact that the uptake of isobutane at 0°C is very slow, as shown from static adsorption experiments.

The reactions involving 3-methyl-1-butene indicate that the diffusion rate of this molecule through the catalyst pores is not significant when compared to 1-butene. Apparently even the relatively flat cyclopentene molecule is able to diffuse into the molecular sieve support more rapidly than 3-methyl-1-butene, again suggestive of slit-shaped pores or constrictions.

The exact effect of intraparticle diffusion on the results reported here is difficult to assess. Effective diffusivities for the various hydrocarbons were not measured and literature values for microporous carbons vary over several orders of magnitude[14, 15]. It is reasonable to assume, however, that considering the small size of the pores in the CCMS–Pt catalyst, as evidenced by the molecular probe results, catalytic selectivity is not strictly a question of whether a molecule can or cannot enter a pore but a matter of relative diffusivities for the reactants involved.

It was noted earlier than the activity of the Engelhard catalyst was much higher than that of the CCMS–Pt catalyst, despite the fact that each material contains close to 1% platinum. This is obviously of importance and may be due to a number of differences in the two materials: (1) total surface area, (2) fraction of the total area covered by platinum, (3) intrinsic activity of the platinum, (4) promoting effects of other impurities on the carbon surfaces and (5) extent of resistance to internal diffusion of reactants and products.

The total surface area of the CCMS–Pt catalyst was significantly less than that of the Engelhard catalyst, that is 180 compared to

1170 m²/g from butane adsorption. Further, the fraction of surface containing platinum would be expected to be considerably smaller for the CCMS–Pt catalyst, because of differences in method of preparation of the two materials. For the CCMS–Pt sample, platinum should be dispersed more uniformily through the solid, that is, it should be both on the available surface and in the bulk. For the Engelhard catalyst, where an impregnation technique is used to add platinum to an already existing microporous carbon, the platinum is expected to reside on the available surface. Clearly the utilization of total platinum should be superior in this latter case.

Little can be said about possible differences in the intrinsic activity of the platinum or the promoting effects of other impurities in the two catalysts on activity. Typical granular activated carbons, including the Barnebey–Cheney carbon used to produce the CCMS–Pt catalyst in this study, have negligible catalytic activity for the hydrogenation reactions studied under the conditions used. Spectrographic analysis of the two samples showed the presence, at about the 1% level, of Si, Mg, and Na in the CCMS–Pt sample and Si, Fe, Al, and Na in the Engelhard sample.

One step in the hydrogenation reactions studied involved the breakage of the hydrogen–hydrogen bond, that is, probably dissociative chemisorption of hydrogen on the platinum surface. We, therefore, studied briefly the relative rates of parahydrogen conversion and hydrogen-deuterium exchange at 150°C over the 2 catalysts. At this temperature, the rates of these reactions are known to be primarily controlled by the rate of hydrogen dissociation. The conversion reaction was 10 times more rapid over the Engelhard catalyst; the exchange reaction was 8 times more rapid.

Differences in activity of the 2 catalysts may also depend on differences in mass transport resistance of reactants and products in the microporous material. Thus, the average size of the micropores (or pore constrictions) in the CCMS–Pt sample is undoubtedly smaller than in the Engelhard sample. The magnitude of the diffusion coefficient for molecules will be less in the micropores of the CCMS–Pt material than in the Engelhard sample. Whether this, in turn, would result in poorer catalyst utilization will depend upon the average length of the micropores leading off of the larger transitional and macropores, where diffusion will be rapid. Obviously, if utilization of the catalyst located on the micropore surface is to be high for molecular sieve supports, the diffusion distance within the micropores must be made small. This is what has been attempted in using the method of sample preparation described briefly here and discussed in more detail elsewhere[12]. That is, carbonization of the polymer causes it to shrink against an expanding (because of thermal expansion) filler, thereby resulting in macrocracking in the polymer carbon and a reduction in diffusion distance within the micropores present in that carbon.

It would be reasonable to assume that when carbon is used as a molecular sieve catalyst support, oxidizing gases should be avoided, particularly at elevated temperatures. Oxidation of the carbon, particularly around pore mouths, could destroy molecular sieve properties, since removal of surface oxides is always accompanied by loss of carbon. Experiments at 100°C, however, have shown that this is not a problem at this low a temperature[16]. That is, admission of air to the catalyst for 1 min resulted in deactivation for 1-butene hydrogenation; but subsequent reduction in hydrogen at 400°C for 15 min restored not only catalytic activity but molecular sieve properties as well. The upper temperature limit for the use of these catalysts in oxidizing atmospheres has not been determined.

In conclusion, the use of carbon molecular sieves as selective catalyst supports

may offer some advantages over other supports, particularly where dual-functionality is undesirable or where the slit-like nature of the pores can be utilized. Many carbon precursors are available and it should be possible to 'tailor' pore sizes for particular reactions. The use of these catalysts in oxidizing atmospheres is possible, at least under certain conditions of temperature and depending on the exact catalyst-reaction system employed.

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