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Propylene Hydrogenation over Platinum/Carbon Molecular Sieve Catalysts

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Studies have been made of the kinetics of hydrogenation of propylene over a catalyst consisting of platinum suspended in a carbon molecular sieve matrix. Rates of adsorption and diffusion of reactants and products in the catalyst have been found to have a controlling influence on the kinetics. Two processes can be identified, one involving fast irreversible adsorption of propylene on metal and one involving slow reversible adsorption in the carbon molecular sieve. Hydrogenation has been found to be dependent on the latter, which has been suggested to be an adsorption/surface diffusion process involving migration through the pores to metal sites.

INTRODUCTION

Considerable interest has been focused on the preparation and characterization of carbons which possess well-defined microporous structures. Carbonization of Saran polymers, for example, has been found to produce carbon with micropores of diameter 6–15 Å (*1*), while polymerized furfuryl alcohol carbonizes to give a solid with micropores of 6–10 Å diameter (*2*). These carbons may be unsupported, or may be combined with a filler carbon to give a higher surface area composite molecular sieve (*3*).

In recent years, the concept of combining such a microporous carbon with a catalyst (*4*, *5*) has been developed. Taking advantage of the fact that the carbon precursors are liquid, Cooper and Trimm have prepared shape-selective catalysts from a variety of materials (*4*): when the active catalyst is suspended within the carbon matrix, the solids only catalyze reactions involving gases small enough to pass through the micropores. The efficiency of such composites depends not only on the inherent activity of the catalyst, but also on their diffusion and adsorption/desorption characteristics. Thus, for example, the efficiency of the catalyst can be improved by using a carbon filler to produce macro-cracks in the solid, which lessen the diffusion pathlength in the micropores (*6*, *7*). However, no systematic investigation of the kinetics of catalytic reactions and their dependence on adsorption, desorption or diffusion in the molecular sieves has been attempted. The present paper describes such an investigation for the hydrogenation of propylene on a platinum/carbon molecular sieve catalyst (Pt/CMS). The shape selectivity of this catalyst has been previously

established (*5*): propylene and propane are small enough to enter the micropores.

Experimental Methods

Carbon molecular sieves were prepared from polymerized furfuryl alcohol using the procedure described previously (*2*). Pt/CMS catalysts were obtained by suspending platinum in the carbon precursor (*4*). Metal salts were obtained spectroscopically pure from Johnson Matthey and Co. Ltd. Hydrocarbon gases and hydrogen were obtained from B.O.C.: the hydrogen was passed over a 0.5% Pd/Al_2O_3 catalyst to remove oxygen and then dried over zeolite at liquid nitrogen temperature.

Gas adsorption experiments were carried out using a Combustion Instruments Mark 2 microbalance operated in the static mode and by standard BET methods. Most catalytic experiments were carried out using an all glass pulsed flow microreactor (*8*) in which a pulse of hydrocarbon, made up with carrier to the required pressure, was injected into a stream of carrier gas, which was either hydrogen or helium. The pulse was then passed either to the reactor, which was maintained at a given temperature (±0.2°K) in an air furnace, or direct to the chromatograph for analysis. The gases were separated on a 3 m column packed with 15% $AgNO_3/C_6H_5CH_2CN$/Silocel at room temperature, and generated a signal by passage through a Gow Mac gas density detector. On occasion it was necessary to split the sample before analysis, in order not to overload the column.

Analysis of products of reaction was complicated by the slow diffusion from the catalyst. Gases emerging from the reactor were passed through a trap packed with glass ballotini and cooled to 78°K for a given time after sample injection. The contents of the trap were then warmed to room temperature and injected onto the chromatograph column.

The catalyst used for all experiments contained 5.7% by weight platinum. Fresh catalyst was activated before use by flushing with nitrogen and heating to 673°K in a flow of pure hydrogen to reduce any metal oxides.

Results

Preliminary investigation showed that hydrogenation was reasonably fast between 373°K and 423°K, but that propane tended to be retained on the catalyst. As shown in Fig. 1, the uptake of propylene was fast, while the amount of propane recovered was very dependent upon trapping time. It was impossible to recover all of the propylene as propane or propylene at 423°K, and the amount retained was independent of flow rate. The residual gas could be removed as propane by heating the catalyst to 672°K, and subsequent experiments were completed with such heating between pulses, the results obtained thereafter being reproducible.

The rate of adsorption of propylene, propane and helium into the catalyst was measured using a static technique. The results, summarized in Fig. 2, show that the adsorption of propylene is ca. 10 times as fast as that of propane, while helium is not adsorbed.

The available metal area of the catalyst was measured by hydrogen and carbon monoxide adsorption in the static adsorption apparatus. Prior to gas adsorption, the catalyst was reduced and evacuated at 673°K (16 hr). Hydrogen or carbon mon-

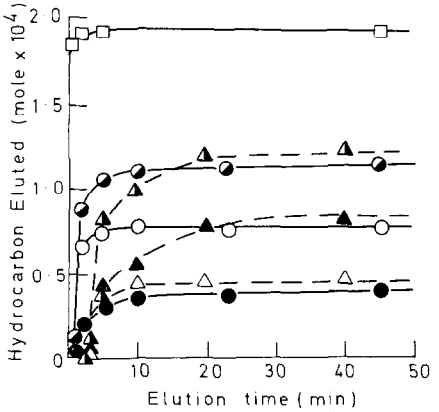

Fig. 1. Elution of reactants and products from Pt/CMS. 1.9×10^{-4} moles propylene/pulse: T = 373°K.

Wt catalyst/flow rate	0	0.024	0.048
Propane		●	▲
Propylene	□	○	△
Total		◑	◭

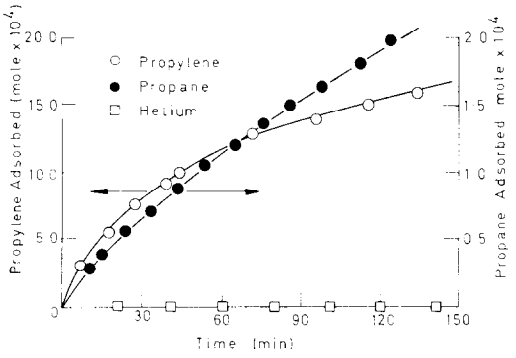

FIG. 2. The adsorption of propylene, propane and helium in Pt/CMS; $T = 423°K$.

oxide was then admitted to the catalyst and the adsorption isotherms were measured: 30 min equilibration times were necessary at each pressure. Typical results are shown in Fig. 3: values obtained at 273° and 298°K were in general agreement with one another.

The amount of hydrogen adsorbed is seen to be ca. six times greater than that of carbon monoxide.

Pulse experiments revealed several unusual features. Measurement of the uptake of propylene with the reciprocal of the space velocity showed that there was a rapid initial uptake of olefin, followed by a slower constantly increasing uptake (Fig. 4). The initial uptake occurred too rapidly to follow, and the plot gave a projected "intercept" and a measured "slope." Examination of the effect of temperature on the uptake showed that the intercept was

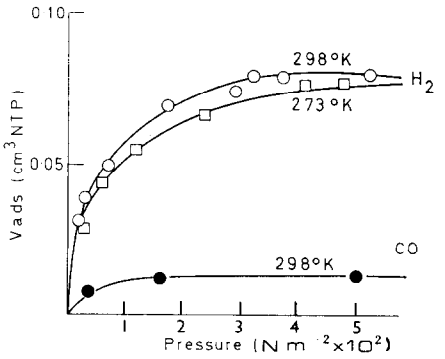

FIG. 3. The adsorption of hydrogen and carbon monoxide in Pt/CMS. Weight catalyst, 1.0 g.

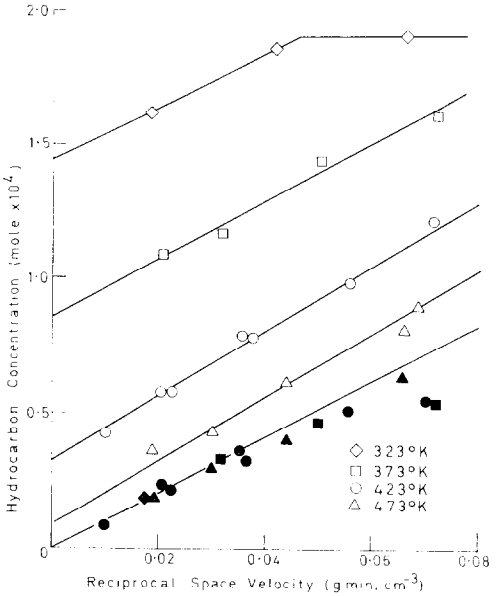

FIG. 4. Propylene hydrogenation as a function of temperature. Propylene = 1.94×10^{-4} moles; open symbols: propylene consumed; closed symbols: propane produced.

temperature dependent but that the slope of the graph, and the production of propane, was essentially temperature independent. The production of propane was measured after trapping the emergent gas for more than 10 min after injection of the sample (Fig. 1).

The effect of pressure on the reaction was studied by varying the partial pressure of olefin in the injected sample: the pressure was adjusted to atmospheric with hydrogen. Since hydrogen is in excess before and after the pulse, and permeates the pores of the catalyst, it is impossible to ascertain the exact concentration of hydrogen and propylene within the catalyst, and the results must be regarded as semi-quantitative. However, a plot of hydrocarbon concentration vs reciprocal space velocity (Fig. 5) projected a positive intercept, which was pressure dependent. The plot obtained at 70 Torr pressure of propylene probably reflects the fact that the catalyst has not been saturated with gas. Diffusion of propane from the catalyst was found to be independent of the initial pressure.

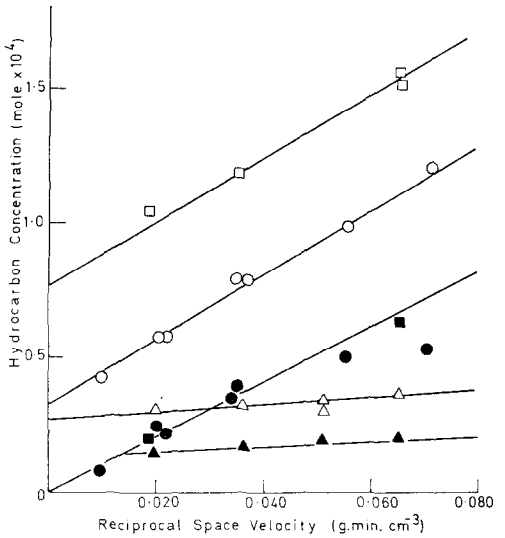

FIG. 5. Propylene hydrogenation as a function of pressure: $T = 423°K$. Open symbols: propylene; closed symbols: propane; (□) 5.6×10^4 N m^{-2}* = 2.85×10^{-4} mole; (○) 3.7×10^4 N m^{-2}* = 1.90×10^{-4} mole; (△) 9.3×10^3 N m^{-2}* = 0.48×10^{-4} mole. * Pressure of propylene in the pulse.

Several experiments were initiated in an attempt to identify the rate determining processes in the reaction. The adsorption of propylene into the catalyst was found to be independent of the pressure of hydrogen (Fig. 6), but to depend upon the presence of platinum. Experiments with the parent carbon molecular sieve showed that the slope of the graph of hydrocarbon concentration vs reciprocal space velocity decreased, and that the intercept disappeared, when no platinum was present (Fig. 6).

The Pt/CMS was then poisoned by passing samples of ethane thiol over the catalyst: this thiol is small enough to enter the pores (*5*) and poisons all the available metal. Subsequent passage of propylene showed that the slope of Fig. 6 was unchanged from the unpoisoned catalyst, but that the intercept of the graph had disappeared (Fig. 6).

DISCUSSION

Preliminary inspection of the results shows clearly that the hydrogenation reaction is influenced by complex mass transfer effects. The observed uptake of propylene by the catalyst is independent of the chemical reaction, as shown by comparison of the rates of adsorption in a hydrogen and a helium carrier (Fig. 6), but the marked differences in rates of uptake of helium, propylene and propane show that adsorption/diffusion must be activated. Recovery of part of the gas after the pulse had passed was facile, but a significant amount of gas was strongly adsorbed, and could only be recovered at high temperatures.

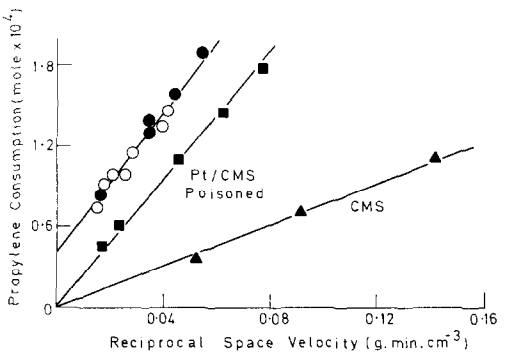

FIG. 6. Propylene hydrogenation on various CMS based catalysts; $T = 423°K$. Propylene = 2.0×10^{-4} moles/pulse; (○) hydrogen carrier; (●) helium carrier.

Two distinct processes can be identified from the plots of propylene uptake vs reciprocal space velocity. One, reflected by the intercept on the plots, is a very fast adsorption which is dependent on the metal function in the catalyst (Fig. 6). The other, reflected by the slope of the plot, is a slow adsorption which occurs independently of the metal. Fairly good correlation can be obtained between intercept values and the amounts of gas strongly adsorbed on the catalyst (compare, for example, Figs. 1 and 4), while the slow adsorption process is reversible. The rates of slow adsorption of propylene and of desorption of propane are the same (Figs. 4 and 5) and are essentially independent of pressure and temperature.

The value of the intercept increases with increasing pressure and decreases with increasing temperature, but appears to be independent of Knudsen diffusion in that no correlation could be established with

predicted temperature dependences (*9*). On the assumption that the fast uptake approaches an equilibrium, values of the intercept at various temperatures were inserted in the Van't Hoff equation and gave an apparent heat of adsorption of 16.75 kJ/mole. No quantitative correlations with pressure were attempted in that the concentrations within the carbon molecular sieves were unknown.

Although the fast uptake of gas is activated and is associated with the metal, the operative process cannot be simple chemisorption. This is seen by comparison of the initial uptake of propylene with the adsorption of other gases (Fig. 3) and from the fact that the value of the apparent heat of adsorption measured from the intercept (16.75 kJ/mole) is much less than the known heat of chemisorption of propylene on platinum (ca. 50 kJ/mole).

Considerable differences are seen between the amounts of propylene, hydrogen and carbon monoxide adsorbed on the catalyst. The total amount of platinum in the catalyst is ca. 2.9×10^{-4} g-atom, of which only 1.6×10^{-7} g-atom is outside the pore structure of the carbon [ascertained by selective poisoning studies using 2,2-dimethyl-propanethiol (*12*)]. The gas adsorption studies show that 6.3×10^{-7} g moles of carbon monoxide, 3.6×10^{-6} g moles of hydrogen and 1.7×10^{-5} g moles of propylene (calculated from the intercept value at 473°K) are adsorbed. It seems possible that carbon monoxide adsorbs only on metal outside the pore system: bearing in mind the smaller molecular size of carbon monoxide, the absorption compares reasonably well with that predicted from thiol poisoning studies. Hydrogen is small enough to enter the micropores of the carbon, and the differences between the adsorption of hydrogen and carbon monoxide may reflect the metal available inside and outside the carbon pore system. In the absence of a reliable value for total metal surface area, this cannot be confirmed. Comparison of the amounts of hydrogen and propylene show, however, that gas adsorption may be further complicated.

The most plausible explanation of these observations would seem to be that the initial uptake of gas involves adsorption on the metal followed by "spillover" of the adsorbed gas onto the carbon surface (*11*). The heat of adsorption observed is of the correct order, and the spillover effect would explain the high adsorption of propylene via the metal as the original adsorption site. In view of the rapid adsorption, the metal sites must be near to the sieve surface and easily accessible to the gas.

The slow uptake of propylene, which is independent of the metal function in the catalyst, seems best explained in terms of surface diffusion into the pores. Surface diffusion is inferred from the non-adsorption of helium, from the similarity in size between the hydrocarbon molecule and the pore width (*5*), and from the relative rates of adsorption of propylene and propane, molecules which are approximately the same size. The carbon pores have been suggested to be bound by graphite layers (*13*), and are known to be only ca. 8×10^{-10} m in width, with small differences between the carbon sieve and the metal-impregnated material (*5*). Propylene should have no difficulty in moving laterally on the pore surface, being kept near to the surface by olefin pi-graphite pi-interaction. Surface diffusion of propane, on the other hand, must involve either the movement across the surface of a "physically" adsorbed species, or some preliminary dehydrogenation to a "chemically" adsorbable state. The dependence of slow adsorption on the pore structure of the carbons, as shown by the differing rates of adsorption on the metal-impregnated and the parent carbon molecular sieve (Fig. 6), rules against the latter possibility. However, in agreement with the experimental observations (Fig. 2), diffusion of "physically" adsorbed propane would be expected to be slower than propylene, in that since the physically adsorbed gas is weakly bound, the molecule will be further from the surface and will have greater difficulty in moving through the narrow pores, particularly were interaction with the pore

wall opposite to the adsorption site is possible.

There is no doubt that propylene hydrogenation is associated with the slow adsorption process, as evidenced by comparison of propylene uptake with propane production (Figs. 4 and 6). Poisoning with a small thiol poisons the accessible metal, stops the hydrogenation and prevents the initial fast adsorption of propylene. Hydrogenation must then be associated with metal sites which are also involved in the initial fast adsorption. However, comparison of propylene uptakes with propane production shows that the hydrogenation itself is not rate determining, but rather it is the activated diffusion of propylene through the carbon pores that controls the observed yields. It is not certain whether this diffusion involves migration within a given pore system to a metal site or migration from a pore that does not contain metal to one that does.

The results show clearly that the stereoselectivity of a catalyst depends not only on the geometric size limitations of the molecular sieve, but also on the rates of adsorption and diffusion in the system. Where surface diffusion is involved, selectivities can be expected to depend markedly on the nature of the gas and the solid. Adsorption/diffusion in the olefin-polyfurfuryl alcohol based carbon molecular sieves is sufficiently fast to provide the basis of a good catalyst.

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