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An IGC Study of Pd/SDB Catalysts for Partial Oxidation of Propylene to Acrylic Acid

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Inverse gas chromatography (IGC) was used to study the interactions of reactants and products with styrene divinylbenzene copolymer (SDB) and Pd supported on SDB catalysts for the propylene partial oxidation to acrylic acid. The adsorption heat, free energies, and specific interaction of propylene, oxygen, water, acrolein, and acrylic acid with the solid surface were measured and compared with *n*-alkane probe molecules. It was found that adsorption of oxygen on Pd/SDB catalysts is very weak, even weaker than methane. Water does not adsorb on the support or the catalyst, but strong adsorption of reaction products, acrolein, and acrylic acid was observed. Based on these results, a mechanism for propylene oxidation over Pd/SDB is proposed.

Key Words: **inverse gas chromatography; hydrophobic catalyst; propylene oxidation; acrylic acid; catalyst characterization.**

INTRODUCTION

During the past decade, the growth in production of solvent-free paints, coatings, and adhesive as well as superabsorbent polymers has resulted in a tremendous demand for acrylic acid. The demand for acrylic acid is expected to increase by 7% per year on a global basis. The current method for manufacture of acrylic acid is a two-stage propylene partial oxidation process. The first step is to oxidize propylene to acrolein using Bi, Mo oxides as catalysts in a temperature range of 330–430°C. The second step is to oxidize acrolein to acrylic acid over Mo oxide catalysts in a temperature range of 280–360°C. Increasing efforts have also been made to develop new catalysts for single-stage partial oxidation of propylene to acrylic acid at low temperatures. Many catalysts have been tested. To date, the most studied catalysts are Pd and most of the reaction was performed in a slurry reactor (1). The activities of these catalysts were generally low and deactivation often occurred after a short time of usage.

We have recently developed a Pd/SDB (styrene divinylbenzene copolymer) catalyst for single-step production of acrylic acid at temperatures below 200°C. This hydrophobic catalyst has shown superior activity compared with traditional hydrophilic supported Pd catalysts. To elucidate the role of hydrophobic support and understand the reaction mechanism over this unique catalyst, information about interactions between reactants (products) and catalyst is very important. This study was undertaken to investigate these interactions using inverse gas chromatography (IGC). Studies on the application of IGC techniques for catalyst characterization are very limited (2, 3), although the techniques have been widely used to characterize polymer-polymer interactions, acid-base interactions, solubility parameters, transition temperature, crystallinity, and surface tension (4). IGC also provides information about the adsorption properties, heats of adsorption, interaction parameters, interfacial energy, and diffusion coefficients (4). Another objective of this study is to extend this technique to catalyst characterization, particularly for polymer-supported catalysts. To quantify the interactions between reactant and catalyst or support, alkanes were also selected as probe molecules in IGC measurements. Based on the IGC and kinetic studies, a reaction mechanism was postulated for propylene partial oxidation over the Pd/SDB catalyst.

THEORY

The theoretical basis of IGC is the same as that of conventional GC. The key parameter for IGC measurements is the net retention volume V_N. The retention volume of the probe molecule depends on the partition of the probe between the stationary phase and the carrier gas, which reflects the bonding strength of probe molecule to catalyst surface. The net retention volume was calculated from (5)

$$V_N = Fj(t_r - t_m)CT, \qquad [1]$$

where F is the uncorrected flow rate detected by bubble flow meter, t_r is the retention time of the probe, t_m is the retention time of nonadsorbing marker (methane), and j is the James-Martin factor for the correction of gas compressibility under pressure difference between column inlet

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(P_{in}) and column outlet (P_{out}) which can be written as

$$j = \frac{3}{2}\frac{\left[\frac{P_{in}}{P_{out}}\right]^2 - 1}{\left[\frac{P_{in}}{P_{out}}\right]^3 - 1} \quad [2]$$

$$C = 1 - P_{H_2O}/P_{out} \quad [3]$$

$$T = \frac{T_{col}}{T_{meter}}, \quad [4]$$

where P_{H_2O} is the water vapor pressure in the bubble flowmeter, T_{col} is the column temperature, and T_{meter} is the temperature of atmosphere.

When adsorption takes place in the Henry's Law region, i.e., at infinite dilution, the standard free energy of transferring 1 mol of probe molecule from the gas phase to the surface at standard state, defined as the variation in the standard free energy of adsorption ΔG_{ads}, can be obtained from (5)

$$\Delta G_{ads} = -RT_{col}\ln\left[\frac{P_{out}V_N}{\pi_0 Sm}\right], \quad [5]$$

where R is the ideal gas constant, π_0 is the spreading pressure of the adsorbed film in the De Boer standard state (338 μN/m), S is the specific surface area, and m is the weight of the packed materials.

The dispersive component of the surface energy (γ_s^D) is given by (6)

$$\gamma_s^d = \frac{1}{4}\frac{\Delta G_{CH_2}^2}{\gamma_{CH_2} N^2 a_{CH_2}^2}, \quad [6]$$

where N is the Avogadro number, a_{CH_2} is the area occupied by a -CH_2- group (0.06 nm^2), and γ_{CH_2} is the surface tension of a surface consisting of CH_2 groups.

$$\gamma_{CH_2} = 35.6 + 0.085(20 - T_{col}) \text{ in mJ} \cdot \text{m}^{-2}. \quad [7]$$

The ΔG_{CH_2} can be calculated from

$$\Delta G_{CH_2} = -RT_{col}\ln\frac{V_{N(n)}}{V_{N(n+1)}}, \quad [8]$$

where $V_{N(n)}$ and $V_{N(n+1)}$ are the retention volume of n-alkanes with (n) and ($n+1$) carbon atoms, respectively. The specific interaction of polar probes, I^{sp}, can be determined from the difference of the free energy of adsorption ($\Delta\Delta G$) between the polar probe and the real or hypothetical n-alkane with the same surface area.

$$I^{sp} = \frac{\Delta\Delta G}{N a_p}. \quad [9]$$

The probe surface area, a_p is calculated from the liquid density and the molecular weight of the probe (7). Although this treatment is empirical, it permits the comparison of the specific interaction between the catalyst and the probe molecules by means of a unified scale.

The adsorption enthalpy (ΔH_{ads}) can be calculated from the Gibbs-Helmholtz equation

$$\frac{\partial\left(\frac{\Delta G_{ads}}{T}\right)}{\partial T} = -\frac{\Delta H_{ads}}{T^2} = -R\frac{d\ln V_N}{dT}. \quad [10]$$

Thus

$$\Delta H_{ads} = -R\frac{d(\ln V_n)}{d\left(\frac{1}{T}\right)}. \quad [11]$$

EXPERIMENTAL

Catalyst Preparation

The 1 wt% Pd supported on SDB was prepared using a conventional impregnation method using $PdCl_2$ as the starting material. The impregnated catalyst was dried under infrared light. The catalyst was reduced at 240°C for 16 h under 100 mL/min H_2 flow rate. Details of the catalyst preparation are described elsewhere (8).

BET Surface Area Measurement

The BET specific surface area and the pore volume distribution of catalysts and SDB supports were determined by nitrogen adsorption at 77 K with an OMNISORP 360 instrument at relative pressure $P/P^0 \leq 0.1$. The external surface areas of both catalyst and SDB support were calculated from the t plot diagram (9).

Inverse Gas Chromatography

About 0.8 g SDB (or Pd/SDB) with 40–60 mesh size were filled into a 1 m length of stainless-steel column with an inside diameter 2.00 mm (o.d. 1/8 inch). To pack the column, one end of the column was plugged with silane-treated glass wool. The same end of the column was attached to a water suction pump. Packing of the catalyst was accomplished with the aid of a mechanical vibrator. The precise weight of SDB (or Pd/SDB) packed in the column was determined from the weight difference between the packed column and empty column. The column was then treated at 200°C overnight under a helium flow rate of 80 mL/min. To avoid detector contamination, the outlet of the column was not connected to the detector during this treatment period.

A HP 5890 Series II gas chromatograph equipped with both FID and TCD and a HP 3396 Series II integrator were used for the measurements. Typically, the temperature was raised from 180 to 240°C during IGC measurements. Helium was used as carrier gas. All n-alkanes and other probe molecules were analytical grade and used as received without further purification. In order to meet the requirement of adsorption at infinite dilution corresponding to zero coverage and GC linearity, a 0.2 to 0.6 μl probe sample was

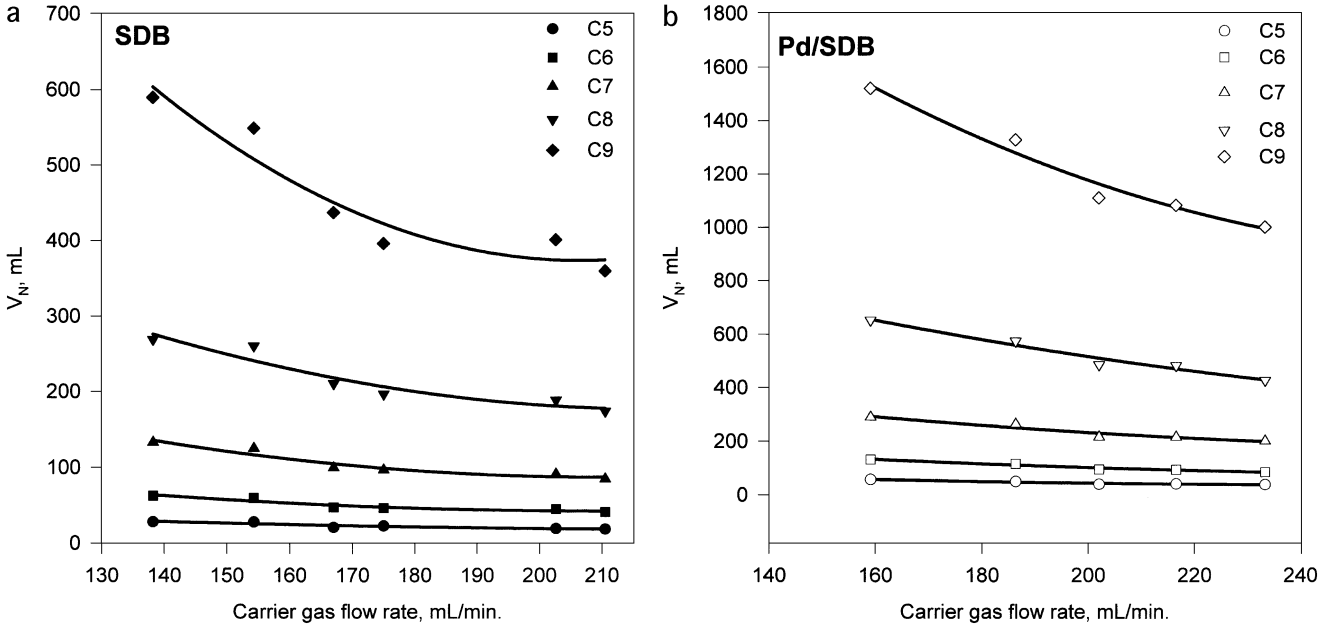

FIG. 1. Influence of carrier gas flow rate on the net retention volume at 180°C.

injected for IGC measurements. For each measurement, at least three repeated injections were taken. Methane was used as a marker for the retention time correction.

RESULTS AND DISCUSSION

Influence of Carrier Gas Flow Rate on the Measurements

The variation of net retention volume of alkanes as a function of carrier gas flow rate with SDB and Pd/SDB as stationary phase at 180°C is shown in Fig. 1. It was noted that for both SDB and Pd/SDB the retention data were sensitive to the carrier gas flow rate. The retention volume of alkanes decreases with increasing carrier gas flow rate and plateaus are observed at higher carrier gas flow rates. Similar results have been reported for both polymers and zeolites (2, 10, 11). It is well understood that the net retention volume should be independent of the flow rate if the measurement is not limited by diffusion effects. To obtain accurate interaction data, it is critical that the influence of diffusion on retention time measurements be eliminated. From Fig. 1 it can be seen that helium flow rates of 180 mL/min for SDB and 210 mL/min for Pd/SDB are needed to eliminate external diffusion limitations under our experimental conditions. All IGC measurements were thus carried out above these critical flow rates.

Interaction of Alkane Probe Molecule with Pd/SDB and SDB

The interaction between catalyst and reactant/product or probe molecule can be attributed to polar or nonpolar (dispersive) Van der Waals forces. It is known that the interaction between alkane, with nonpreferential localization of electrons, and catalyst involved only dispersive forces. The dispersive component of surface energy, ΔG_{CH_2}, can be obtained from the slope of the graph ΔG_{ads} vs the number of carbons for different *n*-alkanes based on Eqs. [5]–[7] (Fig. 2). It was observed that the free energy of adsorption of *n*-alkanes on catalyst increases with the increase in carbon number of *n*-alkanes. Figure 3 shows the temperature dependence of the dispersive component of the surface

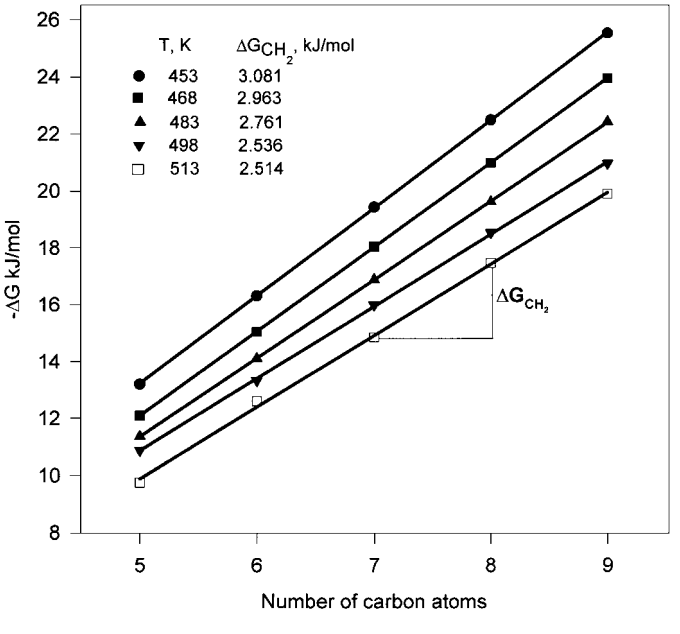

FIG. 2. The free energy of different probe adsorptions on Pd/SDB.

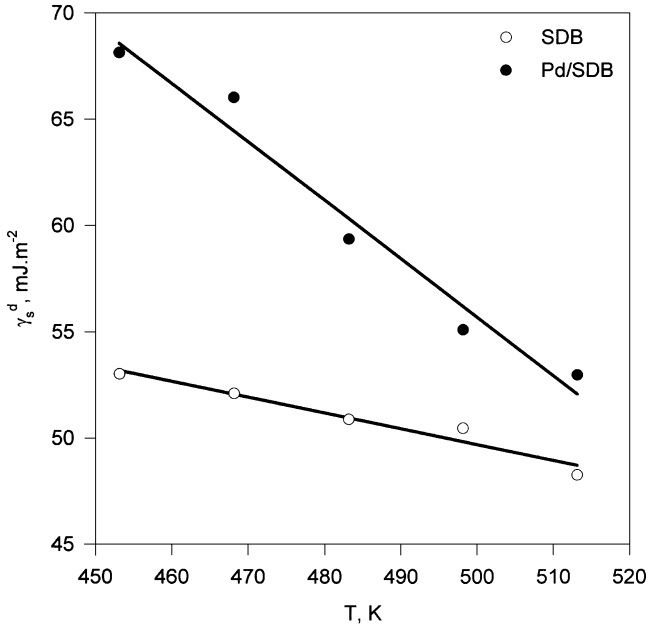

FIG. 3. Dependence of dispersive interaction (γ_s^d) of both SDB and Pd/SDB on temperature.

energy (γ_s^d) for SDB and Pd/SDB samples. In both cases, linear relationships were obtained. It is also noted that the surface free energy of Pd/SDB catalysts is higher than SDB over the temperature range examined. The dispersive component of the surface free energy, γ_s^d is also dependent on temperature. The dispersive interaction decreases with the increase in temperature.

The adsorption enthalpy (ΔH_{ads}) can be obtained from the slope of $R \ln V_n$ vs $1/T$ plot based on Eq. [11] (Fig. 4). The dependence of adsorption enthalpies on the size of probe molecules on both SDB and Pd/SDB is shown in Fig. 5. Linear relationships were observed. It is reasonable that the adsorption enthalpies increase with the increase of carbon number due to the increased interaction between the probe molecule and the catalyst surface. It was also observed that the adsorption enthalpies of *n*-alkanes on Pd/SDB are higher than those on SDB supports. These results clearly indicate the strong interactions between alkane and Pd/SDB, which is in good agreement with the free energy change of *n*-alkane adsorption on Pd/SDB and SDB (Fig. 6). The decrease in the adsorption free energy with the increase in temperature is in agreement with the van't Hoff equation.

Interaction of Reactants and Products with Pd/SDB and SDB

The polar interaction associated with the chemical interaction plays an important role in catalytic reactions. Thus in our study of Pd/SDB catalysts, the reactants, C_3H_6, O_2, H_2O, and products, acrylic acid, and acrolein, were used as probe molecules.

The specific interaction between polar probes (reactants and products) and catalysts or SDB can be calculated from Eq. [8]. The $\Delta\Delta G$ value is the difference of free energy between the polar probe and the real or hypothetical *n*-alkane with the same surface area (Fig. 7). The specific interaction (I^{sp}) between adsorbent (SDB or Pd/SDB) and reactant/product (C_3H_6, acrylic acid, acrolein) at 180°C is shown in Table 1. The retention times for O_2 on both SDB and Pd/SDB were lower than those for methane, thus the thermodynamic parameters of oxygen adsorption on both SDB and Pd/SDB are not given. These results clearly indicate a very weak interaction between oxygen and SDB, Pd/SDB. The free energies of water adsorption on SDB and Pd/SDB are +4.7 and +2.7 kJ/mol, respectively. The positive value of free energy indicates that SDB supports and Pd/SDB catalysts are indeed hydrophobic materials. Our kinetic tests have shown that catalysts with hydrophobic supports have a much higher activity than hydrophilic ones. Since water plays a very important role in propylene oxidation (12, 13), excess amounts of water are present in the reaction system. One factor leading to high activity of the Pd/SDB catalyst for propylene oxidation might be attributed to the lack of liquid film resistance for mass transfer of reactants to the catalyst surface. It is known that the diffusion coefficient in the gas phase is 10^3–10^4 times greater than that in the liquid phase. The adsorption of water on hydrophilic catalysts may inhibit the diffusion and adsorption of propylene on the catalyst, resulting in low activity for hydrophilic catalysts. It is evident that the specific interaction between propylene and Pd/SDB catalyst is higher than that between propylene and SDB. This result indicates that Pd plays an important role in the adsorption of propylene on the catalyst. It was also observed that the specific interaction between SDB and acrylic acid is much higher than that between Pd/SDB and acrylic acid. This result indicates a strong adsorption of acrylic acid on SDB. High specific interaction between catalyst and acrolein was observed which indicates strong adsorption of acrolein on the Pd/SDB catalyst. The strong adsorption of acrolein on catalyst provides the opportunity for further oxidation to acrylic acid and also for polymerization of acrolein. Therefore deactivation of catalyst could occur under some experimental conditions. Indeed polymerization of acrolein at 130°C and

TABLE 1

Specific Interaction (I^{sp}), Free Energy (ΔG_{ads}), and Enthalpy (ΔH_{ads}) of Adsorption

	I^{sp} (mJ · m^{-2})		ΔG_{ads} (kJ · mol^{-1})		ΔH_{ads} (kJ · mol^{-1})	
Probes	SDB	Pd/SDB	SDB	Pd/SDB	SDB	Pd/SDB
C_3H_6	3.5	5.1	−4.1	−6.4	−25.3	−23.4
Acrylic acid	80.9	39.8	−13.3	−8.6	−34.5	−49.7
Acrolein	59.4	67.7	−9.4	−12.4	−35.9	−28.3

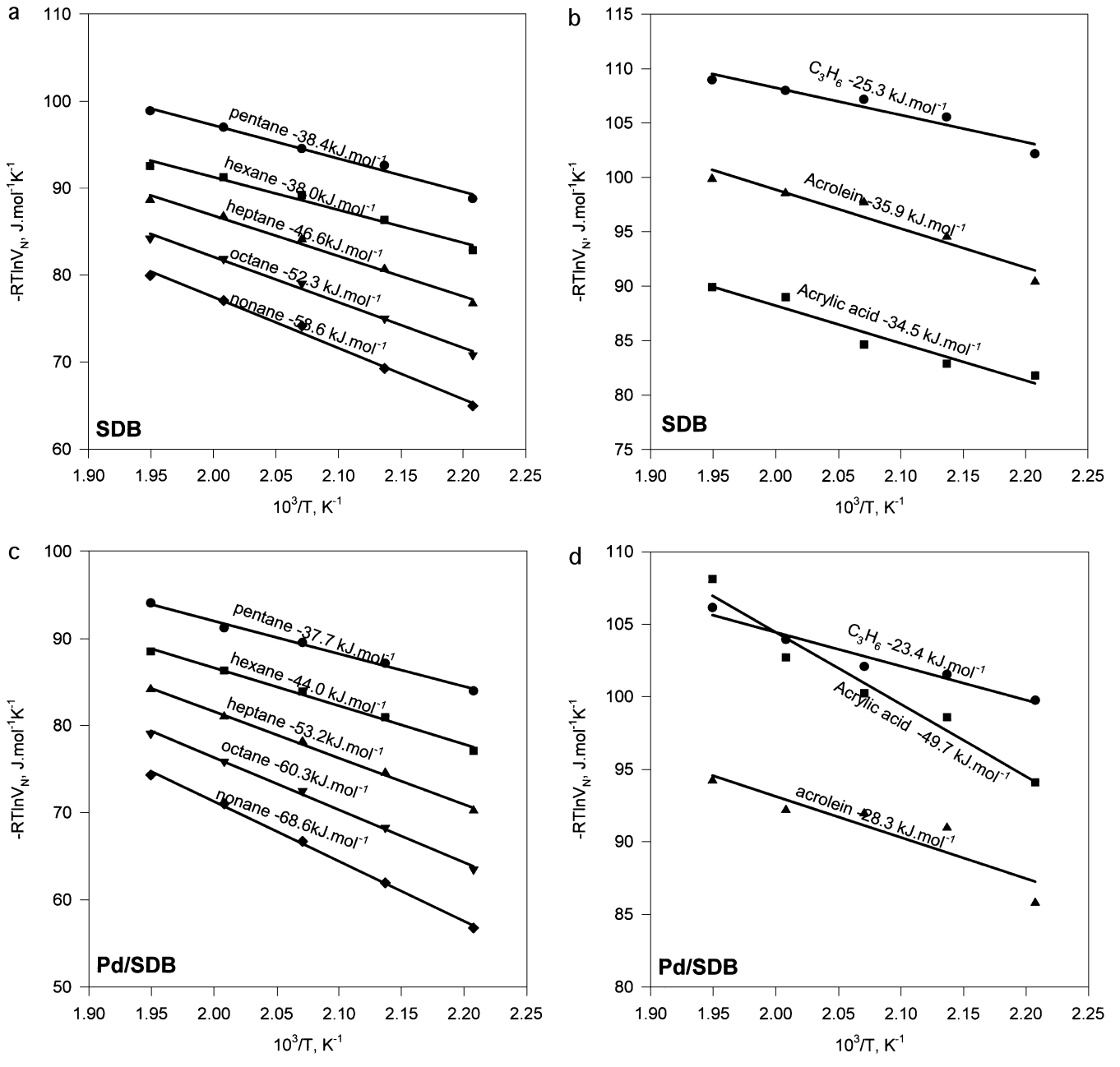

FIG. 4. The determination of adsorption enthalpies of probe molecules on SDB and Pd/SDB.

130 psig was observed in our kinetic tests. As shown in Table 1, the negative free energy and enthalpies of adsorption of propylene, acrylic acid, and acrolein on both SDB and Pd/SDB indicate that the adsorptions of these molecules are spontaneous processes at 180°C.

Mechanism of Propylene Oxidation over Pd/SDB Catalysts

It is well accepted that the first step for propylene partial oxidation over supported Pd catalysts is the adsorption of propylene on catalysts and followed by the activation of a C–H bond of propylene by palladium catalyst to form the π-allyl intermediates (1, 14). The adsorption can be attributed to the electronic localization of propylene on the catalyst. Since propylene, acrylic acid, and acrolein all contain π-bonds, there exists specific interaction resulting from the localization of their electrons. In the kinetic experiments, we observed the production of trace amounts of allyl alcohol. From IGC and kinetic studies, we surmise that water may react only with the π-intermediate formed by propylene adsorption to produce allyl alcohol which is

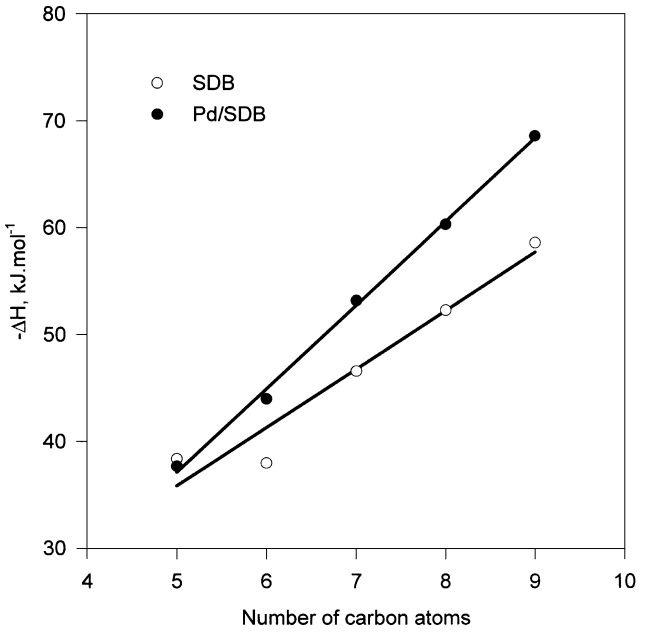

FIG. 5. The adsorption enthalpies of *n*-alkanes on both SDB and Pd/SDB.

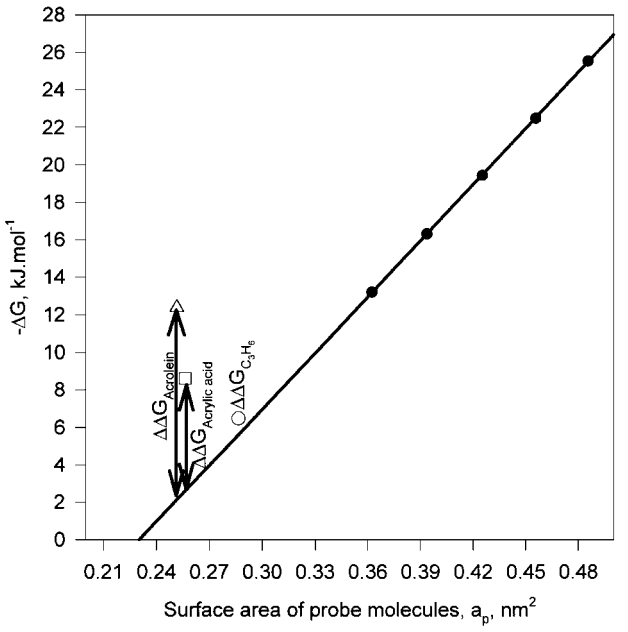

FIG. 7. The determination of specific interaction, Pd/SDB at 180°C.

further oxidized into acrolein. A mechanism for the partial oxidation of propylene to acrylic acid over Pd/SDB catalyst is proposed (Fig. 8). In this mechanism, propylene first adsorbs on the catalyst surface, then the α-H in the methyl group is abstracted by Pd, and the π-allyl intermediate is formed. This π-allyl intermediate reacts with water vapor to form allyl alcohol by neuclophilic attack of H_2O on the π-allyl. The adsorbed allyl alcohol is then activated to form another π-intermediate which reacts with oxygen to form acrolein via oxidative dehydrogenation. The adsorbed acrolein, which contains conjugated π-bond, is activated to form the four atom π-intermediate and the H atom on the carbonyl group is abstracted by catalysts. The adsorbed big π-intermediate then reacts with water molecules to form acrylic acid by nucleophilic attack of H_2O on the carbon atom of the carbonyl group. Oxygen then reacts with the

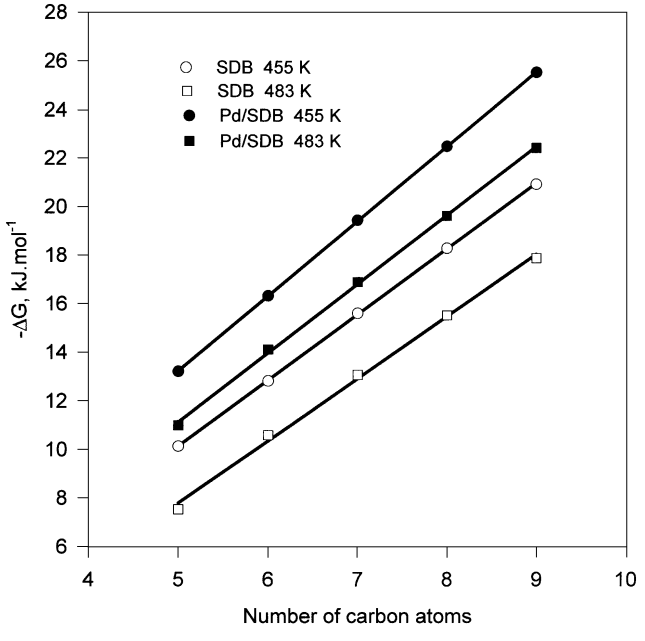

FIG. 6. The adsorption free energies of alkanes on SDB and Pd/SDB at 180 and 210°C.

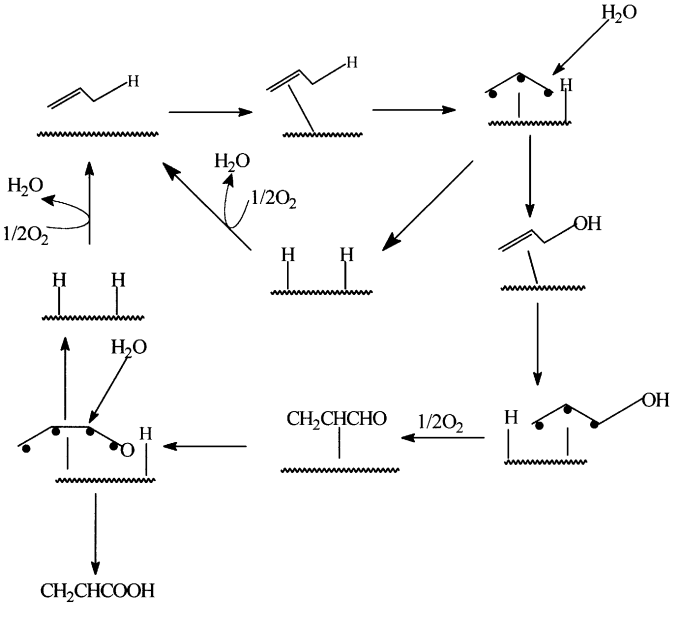

FIG. 8. Scheme of propylene partial oxidation over Pd/SDB.

abstracted H atoms to form H_2O and leaves empty active sites.

CONCLUSION

Inverse gas chromatography has proved to be a very useful technique for study of the interaction of probe molecules with catalysts or supports. The adsorption heat, free energy, and specific interaction of the probe molecule with catalyst can be readily measured. Compared to the interaction of *n*-alkanes as probe molecules, the interaction between oxygen and Pd/SDB catalysts is weaker than that with methane. Pd/SDB is shown to be highly hydrophobic. Pd/SDB-catalyzed propylene partial oxidation involves strong adsorption of reaction products, acrolein, and acrylic acid.

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