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Competitive Hydrogenation of Benzene and Toluene on Group VIII Metals: Correlation with the Electronic Structure

It has been shown previously that the ratio $K_{T/B}$ of the adsorption coefficients of toluene and benzene determined from a kinetic analysis of the competitive hydrogenation of these hydrocarbons can be used to probe the electronic structure of platinum (*1*, *2*). Thus, for 1-nm Pt clusters encaged in zeolites, the changes in the electronic structure induced by the support acidity or by the adsorbates have been monitored with a better sensitivity than by using physical techniques (*1*). Because toluene is more of an electron donor than benzene, the larger the electron deficiency of platinum, the larger the $K_{T/B}$ values. This sensitive chemical probe was also used to detect the formation of Pt–Zr alloys (*2*). The $K_{T/B}$ values decreased linearly upon alloying because, according to the Engel–Brewer theory, there is an electron transfer from Pt to Zr decreasing the Pt *d*-electron population. Finally it has been shown that the different faces of a Pt single crystal are characterized by different $K_{T/B}$ ratios (*3*). Closer values were observed on the (111) and (100) faces ($K_{T/B} = 7$ and 8, respectively) than on the (110) face ($K_{T/B} = 13$). This was related to differences in the electronic structure of these faces (change in work function, surface potential).

In the present work the use of competitive hydrogenation has been extended to other Group VIII metals. This was intended to unveil possible relations between the intrinsic electronic structure of these metals (e.g., the density of states in the *d*-band) and the $K_{T/B}$ ratios. The reactions were carried out on Ru, Rh, Pd, Os, Ir, and Pt. Since previous studies (*1*) have shown that the $K_{T/B}$ ratios are sensitive to modifications of the electronic structure induced by the particle environment, these side effects should be kept as low as possible. Accordingly all the catalysts were prepared on silica which is one of the most inert of supports. The particle sizes were essentially in the range 2–5 nm to minimize potential size effects on the electronic structure. It was also checked that the catalysts contain a negligible amount of sulfur, chlorine, and alkali metals liable to induce electron transfer with the metal. The composition and dispersion of the catalysts are given in Table 1.

The competitive hydrogenation of benzene and toluene was carried out at 298 K on 20–40 mg of catalyst in a conventional flow reactor at atmospheric pressure. The partial pressures of the hydrocarbon were adjusted by two temperature-controlled saturators and by dilution with helium. The benzene and hydrogen pressure were maintained constant ($P_{C_6H_6} = 1$ kPa, $P_{H_2} = 39.5$ kPa) and the toluene pressure varied between 0 and 0.5 kPa. Conversion was less than 10%. The $K_{T/B}$ values were determined as described previously (*1*, *2*) from the slope of the linear transform $V_B^0/V_B = 1 + (b_T/b_B)/(P_T/P_B)$ where V_B^0 and V_B are the ratio of benzene hydrogenation at $P_T = 0$ and P_T variable, respectively, b_T and b_B are the adsorption coefficients ($K_{T/B} = b_T/b_B$) and P_T, P_B are the partial pressures of toluene and benzene, respectively. Figure 1 gives the linear transforms for the different catalysts and the values of $K_{T/B}$ deduced from the slope of the straight lines are collected in Table 1.

The $K_{T/B}$ values vary over a wide range with the nature of the metal. Thus $K_{T/B} \simeq 1$ on Pd/SiO$_2$ which means that benzene is as strongly adsorbed as toluene, whereas $K_{T/B}$

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TABLE 1

Characterization of the Catalysts and $K_{T/B}$ Ratios

Catalysts	Metal (wt%)	Particle size[a] (nm)	Temperature of pretreatment[b] (K)	$K_{T/B}$	C_{el}[c] (mJ mol^{-1} K^{-2})
Ru/SiO_2	5.0	2-5	773	200	3.3
Rh/SiO_2	1.8	2-15	773	10	4.9
Pd/SiO_2	3.7	2-4	673	1	9.4
Os/SiO_2	1.0	>2	773	55	2.4
Ir/SiO_2	3.0	2-4	773	24	3.1
Pt/SiO_2	6.0	>2	673	8	6.8

[a] Measured by TEM (most of the particles are in the range indicated).
[b] Heating in flowing H_2.
[c] Electronic heat capacity of metals (from Ref. (*7*)).

= 55 on Os/SiO_2 corresponding to an overwhelming toluene adsorption on the vacant Os sites. The very high $K_{T/B}$ value on Ru/SiO_2 (≃200) is determined with a large error because benzene hydrogenation at room temperature is completely poisoned by very small increments of toluene in the reactant feed. On this metal, which has a high hydrogenolytic activity, the toluene molecule is probably dissociatively adsorbed via the methyl group even at low temperature in the presence of hydrogen. Note that the formalism of our kinetic analysis of the competitive hydrogenation reaction assumes that the two hydrocarbons are in competition for the same sites and have a similar adsorption mode. Dissociative chemisorption of toluene has been reported for different catalysts under various conditions (*4*). The formation of Ru—C bonds poison the metal surface and hinder the adsorption of benzene which is π-bonded to the surface (*5*). This poisoning is not reversible at room temperature unlike on the other Group VIII metals investigated in this work where the initial benzene hydrogenation activity is recovered when the toluene flow is stopped. This suggests that under our working conditions both reactants are adsorbed via π-bonding albeit with different strength. This is supported by a recent NEXAFS study (*6*) showing that the toluene molecule at room temperature lies flat on the platinum surface exactly as benzene does, but it is tipped after dissociative adsorption at higher temperature. Therefore there is no convincing reason to suspect that benzene and toluene are adsorbed and hydrogenated at separate surface sites with different adsorption modes.

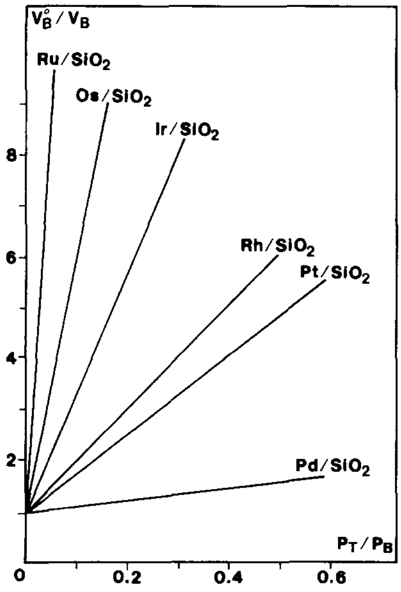

FIG. 1. Plot of the linear transform $V_B^0/V_B = 1 + K_{T/B}(P_T/P_B)$ from the competitive hydrogenation rate of benzene and toluene. The slopes of the straight line give the ratio $K_{T/B}$ of the adsorption coefficients of toluene and benzene.

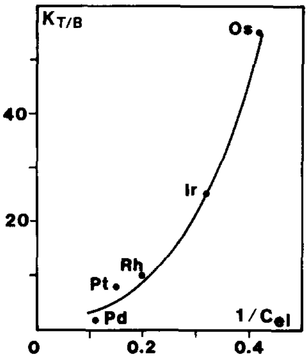

FIG. 2. Ratio of the adsorption coefficients $K_{T/B}$ vs the inverse of C_{el}, the heat capacity of the metal conduction electrons.

The changes in $K_{T/B}$ values observed on the different catalysts can no longer be interpreted in terms of environments or alloying effects as in the previous investigations (*1*, *2*). Instead, they reflect intrinsic changes in the electronic structure of the different Group VIII metals. The bonding of a molecule on a surface depends upon the local density of states on the adsorbing metal atoms. Benzene and toluene are bonded to the metal surface via π bonds involving an electron transfer from the aromatic ring to the unoccupied *d*-metal orbitals. Since toluene is more of an electron donor than benzene as a result of the inductive effect of the methyl group, C_7H_8 is always more strongly bonded than C_6H_6 ($K_{T/B} > 1$) and the lower the density of states at the Fermi level, the higher the $K_{T/B}$ ratios. The local density of states on surface atoms is not available to check such a correlation. However, to a first approximation the density of states at the Fermi level can be represented by C_{el}, the heat capacity of metal conduction electrons, which is related to the density of states $D(\varepsilon_F)$ by the expression $C_{el} = \frac{1}{3}\pi^2 D(\varepsilon_F)k^2T$, where k is the Boltzmann constant (*7*). The C_{el} values are given in Table 1.

The $K_{T/B}$ values have been plotted in Fig. 2 as a function of $1/C_{el}$ for the different metal catalysts except Ru/SiO_2 for which the $K_{T/B}$ ratio is not well established (vide supra). It is noteworthy that the $K_{T/B}$ ratios follow the same order as $1/C_{el}$, namely Pd < Pt < Rh < Ir < Os; therefore, the lower the density of states at the Fermi level (the higher the $1/C_{el}$ values), the higher the $K_{T/B}$ ratios. This correlation supports the oversimplified model of π-electron donation to the *d*-metal orbitals which favors the adsorption of toluene with respect to benzene. Conversely, the measurement of $K_{T/B}$ from competitive hydrogenation of toluene and benzene gives information on the density of states of the metal.

A more complete interpretation of the relation between $K_{T/B}$ and the electronic structure of metals must await further theoretical studies on the chemical bond between the aromatic molecule and the surface metal atoms. The shape of the plot of $K_{T/B}$ vs $1/C_{el}$ (Fig. 2) suggests that a small variation in the density of states, e.g., one induced by an environment effect, will produce a larger variation of $K_{T/B}$ on Ir or Os catalysts than on Pd or Pt catalysts. Accordingly, recent results of competitive hydrogenation performed on a variety of supported iridium catalysts (*8*) show that the $K_{T/B}$ ratio is a much more sensitive probe of the electronic structure on iridium than on platinum.

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TRAN THANH PHUONG[1]
J. MASSARDIER
P. GALLEZOT[2]

Institut de Recherches sur la Catalyse
Laboratoire Propre du CNRS conventionné à l'Université Claude Bernard Lyon I
2 Avenue Albert Einstein
69626 Villeurbanne Cédex
France

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[1] Present address: Laboratory for Catalysis and Petrochemistry, I-Mac Dinh Chi, Ho-Chi-Minh City, Vietnam.

[2] To whom correspondence should be addressed.