Competitive Hydrogenation of Alkyl-Substituted Arenes by Transition-Metal Nanoparticles: Correlation with the Alkyl-Steric Effect

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Abstract: The influence of substituents on rate constants of the hydrogenation of monoalkylbenzenes by transition metal nanoparticles or by classical heterogeneous catalysts can be rationalized in terms of the Taft rule. A series of the initial reaction rate constants obtained from various competitive toluene/benzene and toluene/monoalkylbenzene hydrogenation experiments catalyzed by transition-metal nanoparticles prepared in the presence of imidazolium ionic liquids or surfactants [Ir(0), Rh(0) and Ru(0)] or by classical heterogeneous catalysts (PtO_2, Rh/C, Rh/Al_2O_3, Ru/C, Ru/Al_2O_3 and Pd/C) have been correlated with the Taft equation ($\log\frac{k_B K_B}{k_A K_A} = \rho E_s$). Satisfactory correlation coefficients (r) (between 0.96 and 0.99) and positive slopes (ρ) between 0.38 and 0.83 have been obtained. The results clearly show that the reaction constants for the alkyl-substituents can be expressed by steric factors and are independent of any other non-steric factors. It is suggested that bulky alkylbenzene substituents, for both transition metal nanoparticles and classical heterogeneous hydrogenation reactions, lower the overall hydrogenation rate, implying a more disturbed transition state compared to the initial state of the hydrogenation (in terms of the Horiuti–Polanyi mechanism). This competitive method is suitable for the estimation of the constant selectivity for couples of alkylbenzenes in which the difference in hydrogenation rates are very high and experimentally difficult to measure and also useful for the design of more selective "nano" and classical catalysts for hydrogenation reactions.

Keywords: arenes; hydrogenation; ionic liquids; steric effects; transition metal nanoparticles

Introduction

It is expected that transition-metal nanoparticles of 1–10 nm in size will exhibit physical-chemical properties intermediate between those of the smallest element from which they can be composed and those of the bulk material.[1] The catalyst performance (activity and selectivity) of nanoparticles can be strongly dependent on their size, shape, surface structure and bulk composition.[2] It is evident that the use of physical methods such as EXAFS, TEM, STM, XPS, XRD, etc. can give important information about the structure and composition of transition-metal nanoparticles and allows an understanding at the molecular level of the transformations promoted by these catalysts.[3] However, knowledge of catalyst structure-performance relationships can be also accessed through the use of chemical probes. In particular, the competitive hydrogenation of arenes may allow the assessment of the relation between the molecular structure and the rate of a surface reaction in parallel with the stability of the surface complex in classical heterogeneous catalysts.[4] However, the use of linear free energy relationships (LFER) in heterogeneously catalyzed reactions has found little applications as compared to homogeneous reactions. This is probably related to the fact that the assessment of the electronic or steric effect of the substituent is often difficult; because of the joint action of the heterogeneous catalysts and the reaction conditions, and ultimately it is assumed that the overall effect is determined by both steric and electronic factors.[5] Nonetheless, some interesting conclusions have been obtained, for example, based on the study of the hydrogenation of monoalkylbenzenes over ruthenium black in methanol performed several years ago.[6] It was thus concluded that the reaction rate is independent of electronic effects and the adsorbed state is stabilized by electron-donating substituents,[7] in terms of the Horiuti–Polanyi mechanism (Figure 1).[8]

Furthermore, in classical heterogeneous catalysis the catalyst activity for the hydrogenation of monoalkylbenzenes is lower than for benzene since these large substrates can assume different adsorption modes, includ-

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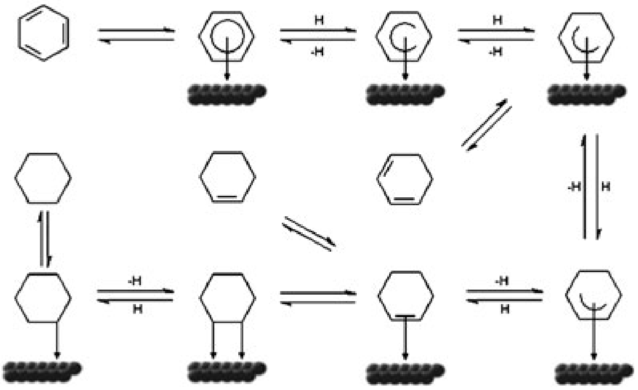

Figure 1. A simplified scheme of the classical Horiuti–Polanyi mechanism for the catalytic hydrogenation of benzene over metal surfaces. The addition of the first two hydrogen atoms is the rate-determining step; the subsequent addition of the four hydrogen atoms is fast.[9]

ing those between the alkyl substituents with the metal surface and/or support that are not suitable for the hydrogenation of aromatic ring.[10] More recently, it was shown that competitive gas phase hydrogenation of benzene (B) and toluene (T) can be used to probe electronic structure of supported nanometric transition metal catalysts.[11] It is assumed in these cases that benzene and toluene are in competition for the same catalytic site and have a similar adsorption mode, i.e., *via* π-bonding to the surface albeit with different strength. It has been thus observed that higher $K_{T/B}$ ratios were attained for the nano-metric metal catalysts investigated (Pd, Pt, Rh and Ir) possessing the lower density of states at the Fermi level.[12] Theoretical studies indicated that the inductive effect of the methyl group is important only if this group is bent away from the surface, otherwise toluene is more difficult to adsorb than benzene due to the steric repulsion existing between the methyl group and the surface.[13]

It is known that soluble transition metal nanoparticles (nanoclusters) differ from classical heterogeneous catalysts and colloids in being 1–10 nm in size, having well-defined compositions, near monodispersed ($\leq 15\%$ size dispersion), reproducible syntheses and catalytic activities, can be re-dissolved, etc.[14] In this respect the advent of more simple and efficient methods for the stabilization of nanoclusters in solution involving electrostatic and/or steric protection by the use of water-soluble polymers, quaternary ammonium salts, surfactants or polyoxoanions has allowed the synthesis of various types of “nanocatalysts”. In most of cases, these nanoparticles are excellent catalysts for the hydrogenation of arenes.[15] However, little is known about the mechanism of this reaction but it is usually assumed that the hydrogenation of arenes by soluble transition-metal nanoparticles follows a similar mechanism as the classical heterogeneous catalyzed reactions. It was thus observed that the hydrogenation of benzene by water-soluble Rh(0) nanoparticles is first order in molecular hydrogen and zero order in benzene.[16]

An intimate knowledge of the structure-reactivity of the substrate(s)-surface of transition metal nanoparticles – compared to classical heterogeneous catalysts – is fundamental for the development and synthesis of more efficient and selective catalysts. The main goal of the present work is to examine the influence of the steric effect in the hydrogenation of monoalkylbenzenes by different non-supported transition metal nanoparticles obtained in ionic liquids or a surfactant and compared to the classical supported heterogeneous catalysts.

Results and Discussion

Initial Considerations

The initial reaction rates of the arene hydrogenation by classical metal heterogeneous catalysts can be expressed by Eq. (1; monomolecular irreversible surface reaction):

$$-\left(\frac{d[Arene]}{dt}\right)_0 = \frac{k_{Arene}K_{Arene}P_H}{1+K_{Arene}[Arene]} \tag{1}$$

where [Arene] is the concentration of the arene, P_H is the pressure of hydrogen, K is the equilibrium adsorption constant and k the kinetic constant and using the competitive method for the hydrogenation of monoalkylbenzenes A and B we obtain:

$$\frac{d[B]}{d[A]} = \frac{k_B K_B [B]}{k_A K_A [A]} \tag{2}$$

then

$$\frac{k_B K_B}{k_A K_A} = \frac{\log(1-X_B)}{\log(1-X_A)} \tag{3}$$

where X_A and X_B are the conversions of arenes A and B, respectively. The ratios $\frac{k_B K_B}{k_A K_A}$, that possess the kinetic and thermodynamic parameters, correspond to the selectivity constant (S_{BA}) according to the concentration of arenes A and B.[17] Moreover, Eq. (2) can be used in a Hammett-relation if

$$\log k_{rel} = \rho_1 \sigma \tag{4}$$

and

$$\log K_{rel} = \rho_2 \sigma \qquad (5)$$

it follows that

$$\log(kK)_{rel} = (\rho_1 + \rho_2)\sigma \qquad (6)$$

which is a linear relationship.[18]

The strategy employed in this study was to investigate the relative reaction rates for the hydrogenation of various monoalkylbenzenes (benzene, toluene, ethylbenzene, isopropylbenzene, *sec*-butylbenzene and *tert*-butylbenzene) by stable transition metal nanoparticles with small diameter and narrow size distribution. The relative reaction rates were obtained by performing competitive reactions between toluene and the other arenes assuming that all catalytically active sites are accessible to both substrates and they are not adsorbed and hydrogenated at separated sites with different adsorption modes. Benzene could not be used as standard for the competitive experiments since it is much more reactive than the highly sterically demanding arenes.

We have chosen Ir(0) nanoparticles prepared by hydrogen reduction of $[Ir(cod)Cl]_2$ (cod = 1,5-cyclooctadiene) and $RhCl_3 \cdot x\, H_2O$ or by controlled decomposition of [Ru(cod)(cot)] (cot = cyclooctatriene) dispersed in 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ionic liquid ([Ir(0)]IL; [Rh(0)]IL and [Ru(0)]IL , respectively)[19–21] and $RhCl_3 \cdot x\, H_2O$ in the presence of a surfactant (Aliquat 336) ([Rh(0)]Surf),[22] that are well characterized monodispersed nanoparticles and catalysts for the hydrogenation of arenes. Moreover, we have also performed the competitive hydrogenation experiments using PtO_2 (Adams catalyst) and classical and commercially available supported heterogeneous catalysts: Rh/alumina; Rh/C; Ru/alumina; Ru/C and Pd/C.

Competitive Hydrogenations: Determination of the Constant Selectivity (S)

First we have performed the competitive hydrogenation of toluene with the other alkylbenzenes catalyzed by [Ir(0)]IL nanoparticles and the results are plotted in Figure 2.

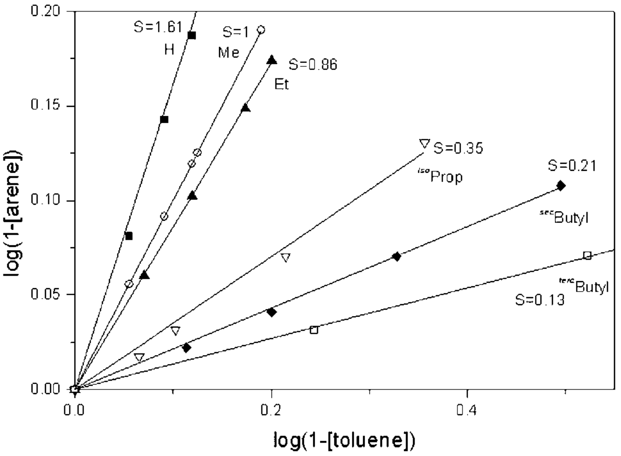

Figure 2. Competitive hydrogenation between toluene and other arenes at 75 °C and 4 atm of hydrogen (constant pressure) by [Ir(0)]IL nanoparticles. The constant selectivity (*S*) is the angular coefficient.

The *S* (ratio $\frac{k_B K_B}{k_A K_A}$) obtained in the competitive experiments using the [Ir(0)]IL nanoparticles and other catalysts are summarized in Table 1. In all cases the correlation coefficient was greater than 0.97 indicating that the ratio of reactivity is constant during the hydrogenation even in the cases where the conversion was almost complete for one of the arenes. However, as expected, higher correlation coefficients were obtained with the decreasing reactivity difference between the two alkylbenzenes used in the competitive experiment. Noteworthy, the ensemble of constant selectivities (*S*) obtained using toluene as the standard can be used for the estimation of any other couple of alkylbenzenes. For example, the calculated *S* (isopropylbenzene/benzene) in the case of [Ir(0)]IL catalyst using the data based on toluene standard (Table 1) is 0.35/1.61 = 0.22, i.e., very close to 0.21 that was measured in a competitive experiment (isopropylbenzene/benzene). This method may be particularly suitable for the estimation of the constant selectivity for couples of alkylbenzenes in which the differences in hydrogenation rates are very high and experimentally difficult to measure (see below).

It is evident that the selectivity constant (*S*) for the hydrogenation of monoalkylbenzene is apparently a function of the steric hindrance of the alkyl group and this is a general trend for the catalysts investigated in this study. It is also clear using the same metal catalyst as for example of rhodium that those based on non-supported nanoparticles ([Rh(0)]IL and [Rh(0)](Surf.)) possess a much higher constant selectivity than those obtained with the supported rhodium catalysts. For example, the calculated *S* (benzene/*tert*-butylbenzene) for the former Rh catalysts is greater than 73 whereas a maximum value of 21 is attained for the classical heterogeneous catalysts.

LFER – Taft–Charton Relations

One of the best ways to express the steric effect imposed by different alkyl groups and correlate with kinetic data is the Taft E_s values[23] that are shown to be a linear function of the van der Waals radii and independent of electrical effects.[24] We have also plotted the competitive results ($\log(\frac{k_B K_B}{k_A K_A})$) against the Charton parameter (ν) that

Table 1. Competitive hydrogenation between toluene and other arenes at 75 °C and 4 atm of hydrogen (constant pressure) by some metal catalysts showing the constant selectivity (S).

Arenes/Catalyst	[Ir(0)]IL	[Ru(0)]IL	[Rh(0)]IL	Rh/C	[Rh(0)]Surf.	Rh/Al$_2$O$_3$	Ru/Al$_2$O$_3$
Benzene	1.61	3.41	5.11	2.80	5.13	3.45	4.00
Toluene	1	1	1	1	1	1	1
Ethylbenzene	0.86	0.73	0.73	0.94	0.65	0.92	0.95
Isopropylbenzene	0.35	0.28	0.30	0.32	0.17	0.51	0.32
sec-Butylbenzene	0.21	0.17	0.14	0.20	0.07	0.35	0.19
tert-Butylbenzene	0.13	0.11	0.07	0.16	0.05	0.12	0.11

Table 2. Relative initial reaction rate for the hydrogenation of toluene and various alkylbenzenes by various metal catalysts ($k_{rel.} = \frac{k_B K_B}{k_A K_A}$).

Entry	Alkyl	Charton (ν)	Taft (E_s)	log $k_{rel.}$ [Ir(0)]IL	log k_{rel} [Ru(0)]IL	log k_{rel} [Rh(0)]IL	log k_{rel} Rh/C	log k_{rel} [Rh(0)]Surf	log k_{rel} Rh/Al$_2$O$_3$	log k_{rel} Ru/Al$_2$O$_3$	log k_{rel} Ru/C	log k_{rel} Pd/C	log k_{rel} PtO$_2$
1	H	−0.04	1.24	0.301	0.477	0.70	0.48	1.00	0.544	0.620	0.342	0.447	0.447
2	Me	0	0	0	0	0	0	0	0	0	0	0	0
3	Et	0.12	−0.07	−0.12	−0.30	−0.17	−0.07	−0.17	−0.079	−0.080	−0.263	0.032	−0.062
4	*i*-Pr	0.20	−0.47	−0.48	−0.42	−0.55	−0.46	−0.70	−0.602	−0.367	−0.324	−0.376	−0.602
5	*s*-Bu	0.46	−1.13	−0.60	−0.72	−0.93	−0.65	−1.07	−0.832	−0.720	−0.556	−0.637	−0.860
6	*t*-Bu	0.68	−1.54	−0.98	−0.95	−1.28	−0.70	−1.20	−0.954	−0.884	−0.662	−0.669	−1.146

takes on a consideration of the van der Waals radii and Taft E_s values.

The resulting Taft plot ($\log(\frac{k_B K_B}{k_A K_A})$ as a function of E_s) is exhibited in Figure 3. The use of E_s constants results in a satisfactory fit (r = 0.97) and correlation yields a value of a slope 0.46 indicating that the overall reaction rate for the hydrogenation of alkylbenzenes is dependent on the steric hindrance of the alkyl group.

The same protocol of competitive experiments has been used with different catalysts and their $\log(\frac{k_B K_B}{k_A K_A})$ were plotted against the Taft and Charton parameters and the results are summarized in Tables 2 and 3. It is clear that for all catalysts the $\log\frac{k_B K_B}{k_A K_A}$ correlates well with the Taft and Charton parameters indicating that in these cases too the hydrogenation reaction of mono-alkylbenzenes are sensitive of steric effects. The slope (ρ) varies from 0.38 in the case of Ru/C (Table 3, entry 5) to 0.82 in the case of [Rh(0)]Surf. (Table 3, entry 8). Noteworthy is that the significance of the deviation of points of a Hammett–Taft plots from the regression line depends both on the experimental error and on the value of ρ. The correlation coefficient (r) decreases with increasing of the slope (ρ) and r values between 0.96 and 0.99 can be considered in our case satisfactory.[25]

In the case of rhodium catalysts those supported in carbon or alumina (Table 3, entries 6 and 7, respectively) the hydrogenation reactions of alkylbenzenes are less sensitive to steric effect than those performed with nanoparticles prepared in 1-*n*-butyl-3methylimidazolium hexafluorophosphate ionic liquid or Aliquat-386 (Table 3, entries 2 and 8, respectively). Most

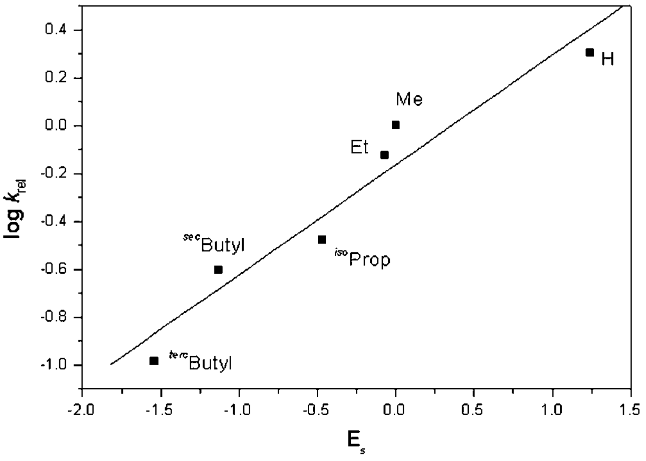

Figure 3. The relation between substituents parameters (E_s) and the relative reaction rate constants ($\frac{k_B K_B}{k_A K_A}$) for the competitive hydrogenation of toluene and other arenes over [Ir(0)]IL nanoparticles (75 °C, 4 atm of H$_2$).

Table 3. Correlation coefficients (r) and slope (ρ) obtained from $\log\frac{k_B K_B}{k_A K_A} = \rho E_s$ in the hydrogenation of alkylbenzenes by different catalysts.

Entry	Catalyst	Taft		Charton	
		r	ρ	r	ρ
1	[Ir(0)]IL	0.96	0.46	0.97	–1.04
2	[Rh(0)]IL	0.99	0.72	0.99	–1.62
3	[Ru(0)]IL	0.98	0.51	0.98	–1.15
4	Ru/Al$_2$O$_3$	0.99	0.56	0.99	–1.25
5	Ru/C	0.98	0.38	0.99	–0.87
6	Rh/C	0.98	0.45	0.98	–1.10
7	Rh/Al$_2$O$_3$	0.98	0.57	0.98	–1.30
8	Rh(0)/Surf.	0.98	0.82	0.98	–1.86
9	PtO$_2$	0.97	0.60	0.97	–1.35
10	Pd/C	0.97	0.43	0.98	–0.97

importantly, for all catalysts the augmentation of the size of the alkyl substituents decreases the overall reaction rate that may be related in a more disturbed transition state as compared to the initial state of the hydrogenation.[7]

Conclusion

We have demonstrated that the competitive hydrogenation of alkylbenzenes can be used for the determination of the constant selectivity of transition metal nanoparticles and these constant selectivities obtained against toluene can be used for the prediction of the relative reactivity of any other couple of monoalkylbenzenes. The initial reaction rate constants obtained from various competitive toluene/benzene and toluene/monoalkylbenzene hydrogenation experiments catalyzed by transition metal nanoparticles or by classical heterogeneous catalysts can be correlated with the Taft equation ($\log\frac{k_B K_B}{k_A K_A} = \rho E_s$). Therefore the relative reaction constants for the alkyl substituents can be expressed by steric factors and are independent of any other non-steric factors. It is suggested that bulky alkylbenzene substituents, for both transition metal nanoparticles and classical heterogeneous hydrogenation catalysts, lower the overall hydrogenation rate, implying in a more disturbed transition state as compared to the initial state of the hydrogenation (in terms of the Horiuti–Polanyi mechanism). Finally, the competitive hydrogenation of monoalkylbenzenes can be used as a chemical probe to quantitatively compare the selectivity and the steric influence imposed by different types of metal catalysts. This method may provide a complementary tool for the evaluation of the interactions substrate(s)-surface of transition metal nanoparticles and, more important, it may be very useful for the design and synthesis of more efficient and selective hydrogenation catalysts.

Experimental Section

General Remarks

All reactions involving iridium, rhodium and ruthenium compounds were carried out under argon atmosphere in oven-dried Schlenk tubes. The BMI[PF$_6$] ionic liquid was prepared according to a known procedure,[26] dried over molecular sieves (4 Å) and its purity was checked by an AgNO$_3$ test, ^{1}H and ^{31}P NMR, and cyclic voltametry. The water (<0.1 wt %) and chloride[27] (<1.4 mg/L) contents in the BMI[PF$_6$] were determined by known methods. Solvents and arenes were dried with adequate drying agents and distilled under argon prior to use. All the other chemicals were purchased from commercial sources and used without further purification. [Ir(cod)Cl]$_2$, Rh/Al$_2$O$_3$ (5%), Ru/C (5%) and Ru/Al$_2$O$_3$ (5%) was purchased from Strem Chemicals; Rh/C (5%) and Pd/C (5%) were acquired from Degussa S.A; RhCl$_3\cdot$x H$_2$O from UMICORE Brazil Ltda., PtO$_2$ (Adam's catalyst) was purchased from ACROS.

The formation of nanoparticles and hydrogenation reactions were carried out in a modified Fischer–Porter Bottle immersed in a silicon oil bath and connected to a hydrogen tank. The fall in the hydrogen pressure in the tank was monitored with a pressure transducer interfaced through a Novus converter to a PC and the data worked-up *via* Microcal Origin 5.0. The temperature was maintained at 75 °C by a hot-stirring plate connected to a digital controller (ETS-D4 IKA). A deliberate stirring at 800 rpm was used.

Characterization Measurements

Mass spectra were obtained using a GC/MS Shimadzu QP-5050 (EI, 70 eV). Gas chromatography analyses were performed with a Hewlett-Packard-5890 gas chromatograph with an FID and 30-meter capillary column with a dimethylpolysiloxane stationary phase (T_i 70 °C – 7 min, rate = 15 °C/min, T_f 250 °C – 10 min, $P=5$ psi). The X-ray diffraction was performed in a Philips X'Pert MRD diffractometer in a Bragg–Brentano geometry using curved graphite crystal as monocromator. Transmission electron microscopy (TEM) was performed on a JEOL 2010 microscope operating at 200 kV. The TEM images were obtained in bright-field conditions using a 20 μm objective aperture and with the objective bus slightly underfocused ($\Delta f \sim 500$ nm).

Iridium Nanoparticles

In a Fischer–Porter Bottle containing a yellow solution of [Ir(cod)Cl]$_2$ (16 mg, 0.05 mmol) in dichloromethane (3 mL) was added BMI[PF$_6$] (1 mL) and the mixture stirred at room temperature for 15 min. The volatiles were then removed under reduced pressure (0.1 bar) at 75 °C for 1 h. The system was kept at 75 °C and hydrogen (4 bar) was admitted to the system. After stirring for 10 min a black "solution" was obtained from which the Ir nanoparticles were isolated by centrifugation (3000 rpm) for 5 min, washed with acetone (3 × 5 mL) and dried under reduced pressure. The Ir samples thus obtained were prepared for TEM and X-ray analysis, and for catalytic experiments (see below). TEM micrographs showed that the iridium nanoparticles possess a diameter of 2.0 ± 0.5 nm.

Ruthenium Nanoparticles

In a typical experiment, a Fischer–Porter bottle containing a yellow suspension of [Ru(cod)(cot)][28] (92.5 mg, 0.3 mmol) in 7 mL of BMI[PF_6] was treated with 4 bar of H_2 at 75 °C to afford a black solution after stirring for 18 h. The Ru nanoparticles were isolated by centrifugation (3000 rpm) for 30 min, washed with water (5 × 5 mL) and acetone (5 × 5 mL), and then dried under reduced pressure. TEM analysis showed that the ruthenium nanoparticles have a diameter of 2.6 ± 0.4 nm.

Rhodium Nanoparticles

In a typical experiment, a Fischer–Porter bottle containing a red solution of $RhCl_3 \cdot 3\,H_2O$ (26 mg, 0.1 mmol) in dichloromethane (3 mL) was added to BMI[PF_6] (1 mL) and stirred at room temperature for 15 minutes. The volatiles were then removed under reduced pressure (0.1 bar). The system was kept at 75 °C and hydrogen (4 bar) was admitted to the system. After stirring for 1 h, a black "solution" was obtained that was used for the hydrogenation reactions. The Rh nanoparticles were isolated by centrifugation (3000 rpm) for 5 min, washed with acetone (3 × 5 mL) and dried under reduced pressure. TEM analysis showed that the rhodium nanoparticles have a diameter of 2.7 ± 0.4 nm.

$RhCl_3$-Aliquat 336 Catalyst ([Rh(0)]Surf.)

The [Rh (0)]Surf. catalyst was prepared following the method A from the literature procedure.[22]

Competitive Hydrogenations Experiments

The isolated nanoparticles (0.026 mmol) were placed in a Fischer–Porter bottle and the ratio substrate/catalyst = 250 were maintained by adding 3.25 mmol of each substrate. The reactor was placed in an oil bath at 75 °C and hydrogen was admitted to the system at constant pressure (4 atm). Samples (less than 10 μL) for GC and GC-MS analysis were also removed from time to time under H_2.

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