The role of solvent in heterogeneous catalysis: A comprehensive approach for hydrogenation reactions

C.R. Apesteguía, *N.M. Bertero, A.F. Trasarti. A.J. Marchi*

Catalysis Science and Engineering Research Group (GICIC), Instituto de Investigaciones en Catálisis y Petroquímica, UNL-CONICET, Sgo. del Estero 2654, (3000), Santa Fe, Argentina

Introduction

The synthesis of fine chemicals over solid catalysts often involves the use of solvents that may strongly influence the catalyst performance. Thus, the choice of suitable solvents is frequently critical to obtain high catalytic activity and selectivity. However, the optimal solvent selection requires a detailed knowledge on the relationship between the chemical nature of the solvents and the interactions taking place in the gas-liquid-solid catalytic systems. One of the most common types of catalytic reactions carried out in the presence of solvents is the hydrogenation of organic compounds. In particular, the selective hydrogenation of aromatic ketones into the corresponding alcohols on metal-based catalysts in the presence of different solvents has been widely studied. Here, the solvent effect on catalyst activity and selectivity for the liquid-phase hydrogenation of acetophenone (AP) to 1-phenylethanol (Figure 1) was thoroughly investigated over Ni/SiO_2. Solvents of different properties and polarities were used: i) protic solvents: methanol (MeOH), ethanol (EtOH), 1-propanol (1-PrOH) and 2-propanol (2-PrOH); ii) aprotic polar solvents: acetonitrile (ACN), γ-butyrolactone (GBL) and tetrahydrofuran (THF); iii) aprotic apolar solvents: cyclohexane (CHX), toluene (TOL) and benzene (BZN). The relative interactions solvent–catalyst, solvent–reactant and reactant–catalyst and their influence on the activity pattern were considered in the analysis. Concerning the influence of the solvent-reactant interaction, classical polarity parameters (e.g. dipole moment μ and dielectric constant ε) and other solvatochromic scales (e.g. hydrogen-bond donor (α) and hydrogen-bond acceptor (β) parameters, π* polarity/polarizability index, Kosower's Z and ET(30) scales) were taken into account (Table 1). The influence of H_2 solubility in the solvents was also considered. For the solvent-catalyst and reactant-catalyst interactions, the corresponding molar adsorption enthalpies were measured calorimetrically and compared.

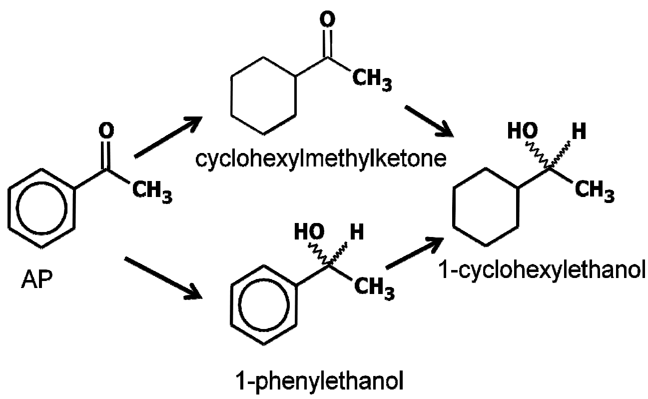

Figure 1: Acetophenone hydrogenation

Results and Discussion

The solvent chemical nature strongly affected the catalytic activity for the liquid-phase AP hydrogenation on Ni/SiO_2, but did not modify significantly the selectivity to 1-phenylethanol that was always higher than 92%. The AP hydrogenation activity followed the order (Figure 2): C_2–C_3 alcohols > cyclohexane > toluene > tetrahydrofuran > γ-butyrolactone > methanol >> benzene ≈ acetonitrile It was not possible to find a global satisfactory explanation for this activity pattern by

Table 1: AP and solvent polarity parameters

Solvent	ε	μ (Debye)	Z	$E_T(30)$ (Kcal/mol)	π*	α	β
2-PrOH	19.9	1.66	76.3	49.2	0.48	0.76	0.84
1-PrOH	20.1	1.68	78.3	50.7	0.52	0.84	0.90
EtOH	24.6	1.69	79.6	51.9	0.54	0.86	0.75
CHX	2.02	0.00	60.1	30.9	0	0	0
TOL	2.38	0.37	56.1	33.9	0.54	0	0.11
THF	7.58	1.63	58.8	37.4	0.58	0	0.55
GBL	39.0	1.43	-	44.3	0.87	0	0.49
MeOH	32.7	1.70	83.6	55.4	0.60	0.98	0.66
BZN	2.28	0.00	54	34.3	0.59	0	0.10
ACN	37.5	3.92	71.3	45.6	0.75	0.19	0.40
AP	17.4	2.9	-	40.6	0.90	0.04	0.49

considering a unique type of interaction with the solvent. In the case of apolar solvents, the main factor influencing catalyst activity was the solvent-catalyst interaction; specifically, the AP hydrogenation rate diminished with the strength of the solvent adsorption on the metal surface. In some cases, solvent adsorption on the metal surface was so strong (e.g. with benzene) that the Ni active sites were blocked and the reaction was completely inhibited. The solvent-AP interactions were weak when using apolar solvents and thereby had negligible effects on catalyst activity.

For aprotic polar solvents, the relationship between catalyst activity and solvent adsorption strength was qualitatively similar to that verified when using apolar solvents, i.e. the AP hydrogenation rate diminished as the solvent adsorption enthalpy on the metal surface increased. However, if apolar and aprotic polar solvents of similar adsorption strength are used, then the AP hydrogenation rate is lower for the aprotic polar solvent. This is because the solvent-AP interaction is stronger for aprotic polar than for apolar solvents, which increases the AP solvation degree, and consequently hinders the AP adsorption on the catalyst surface.

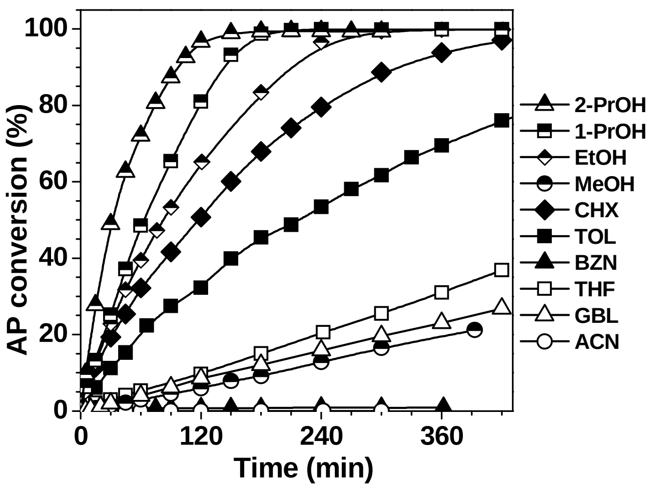

Figure 2: Solvent effect on acetophenone hydrogenation over Ni/SiO_2

The catalyst activity for AP hydrogenation when using protic solvents such as C_1-C_3 alcohols depended on both the carbon chain length and the type of alcohol. Protic solvents are able to interact in liquid phase with acetophenone through hydrogen bond, which strongly solvates the AP molecule. Considering the solvent ability for H-bond formation and other polarity parameters, the AP solvation in protic alcohol solvents would increase following the order: 2-propanol < 1-propanol < ethanol <methanol. This is exactly the opposite trend observed for the AP hydrogenation rate because the reactant adsorption on the catalyst becomes more difficult as the solvation increases.

The highest AP hydrogenation rates were obtained using protic C_2–C_3 alcohol solvents. This superior catalyst activity for AP hydrogenation is explained on the basis of: (i) the dissociative chemisorption of alcohols over the metal nickel surface, which increases the amount of reactive chemisorbed hydrogen; (ii) the polarization and activation of the C=O bond of AP molecule due to its interaction with alcohol molecules through H-bond.