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Hydrogenation of Benzene over Alumina-Supported Nickel Catalysts Prepared from Ni(II) Acetylacetonate

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Hydrogenation of benzene was used to probe the activity of Ni/Al_2O_3 catalysts with metal content in the 0.4–3 wt% range prepared with Ni acetylacetonate as a precursor. Average particle sizes in the 1.9–8 nm range were determined from hydrogen chemisorption measurements depending on the nickel content and reduction temperature. A preliminary decomposition of the organic ligands in air at 250°C followed by reduction markedly increased the activity relative to a direct reduction. Treatments at higher temperatures had a detrimental influence on catalyst efficiency. Catalysts reduced at 350–400°C were more active than those reduced at 450°C and above, with the most active catalysts having nickel content of 1 and 1.6%. The dependency of the turnover frequency on particle size suggested that the reaction was structure sensitive for particle sizes below 4 nm and insensitive above this size. The fraction of unreduced nickel also had an effect on the activity. From a tentative comparison of the turnover frequencies (TOF) with values reported in the literature, it may be inferred that Ni(acac)$_2$ is a rather valuable precursor in preparing very efficient and stable catalysts with low nickel content. © 2001 Academic Press

Key Words: **benzene hydrogenation; nickel acetylacetonate; α-alumina; TOF.**

INTRODUCTION

Hydrogenation of aromatics has become a key parameter in the upgrading processes of middle distillates due to stringent regulations on the level of these compounds in diesel fuels (1, 2). Several refineries adopted the Ben-Sat process (UOP) to reduce benzene in gasoline. Other refineries favored the Tenex-Plus process, combining hydrogenation and isomerization to increase the octane number. In recent years, several vapor-phase hydrogenation processes have been developed (3). Benzene hydrogenation has also been chosen as a model reaction for the characterization of the metal catalysts used in the upgrading of aromatic hydrocarbons derived from coal liquefaction (4–6). More generally, this reaction has been largely used to probe the activity of catalysts for reactions taking place on metal surfaces and to determine the metal surface area available under reaction conditions where metal–support interactions are involved (7).

The use of the turnover frequency (TOF) to quantify the reaction rates constituted one of the key steps in bringing heterogeneous catalysis to its current level of understanding. However, the measurement of a true turnover rate is difficult to establish, owing to the uneasy determination of the concentration of the active sites (8, 9). TOF values obtained for similar catalysts at various laboratories may differ, indeed, by several orders of magnitude (9, 10). Benzene hydrogenation was initially classified as structure insensitive (little variation of TOF with particle size) (10, 11–13), but some catalytic systems, in particular the nickel-based catalysts, have shown structure sensitivity (6, 14–19), leaving the question open. One of the difficulties is that in most of these works, the particle sizes varied over a wide range of values, sometimes well above the range (1–10 nm) wherein the relative percentage of the surface atoms with different coordination numbers varies (20). Above this range, the particles should essentially exhibit bulk behavior and no further change of the catalytic activity is expected (11).

This work is a part of a systematic study on the use of nickel acetylacetonate, a precursor barely investigated for the preparation of Ni/Al_2O_3 catalysts with low metal content. Transition metal-β-diketonates possess a number of important technological advantages, which make them interesting catalyst precursors. They are commercially available, soluble in several organic solvents, stable in normal conditions, and susceptible to undergoing ligand substitution under mild conditions (21). The complex employed must show a strong affinity with the surface which, in turn, will ensure monolayer coverage (22). Aspects related to the adsorption of Ni(acac)$_2$, the thermal decomposition of the organic ligands, and the behavior under reducing conditions have been previously addressed (23–26). The results

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have shown that the use of this precursor constitutes an interesting new route to the preparation of supported nickel catalysts. This study complements the previous studies by examining the catalytic properties of these new catalysts in benzene hydrogenation, the choice of this reaction being dictated both because of its wide use as a model reaction for supported nickel catalysts and for practical considerations. In particular, the influence of the nickel content and the activation conditions on the catalytic activity has been addressed. In order to assess the benefit of using nickel acetylacetonate for the preparation of supported Ni catalysts with low metal content, the turnover frequencies (TOF) established at different temperatures have been tentatively compared with reported values obtained over similar catalysts prepared with inorganic nickel precursors.

EXPERIMENTAL

The support (from Rhône-Poulenc) was majoritary an α-alumina with trace amounts of κ and θ transition phases identified by XRD (25), with a BET specific surface area of 42 $m^2\ g^{-1}$, and a total pore volume of 0.21 $cm^3\ g^{-1}$. Designated quantities of $Ni(acac)_2 \cdot 2H_2O$ (fraction smaller than 100 μm, from Merck), corresponding to Ni contents of 0.4, 1.0, 1.6 and 3 wt%, were dissolved in benzene (UCB, highest purity) under stirring for 15 min and added to calculated weights of the support (fraction smaller than 100 μm) freshly calcined at 500°C for 16 h, with a solution/support ratio corresponding to 10 times the pore volume (2.1 ml g^{-1}). After the slurries were stirred for 48 h at room temperature and filtered, the solids were washed several times with benzene (total volume: 25 ml g^{-1}) and dried at room temperature. Decomposition of the organic ligands was achieved (unless otherwise specified) at 250°C in static air for 4 h. Metal reduction was performed at 400 and 550°C (unless otherwise indicated) in flowing hydrogen (100 ml min^{-1}) for 2 h, with a ramp of 10°C min^{-1}, using Oxy-trap and Hydro-purge (from Alltech Associates) to remove traces of oxygen and water.

The metal dispersion (D, in %) and the metal particle size (d, in nm) were determined from H_2 adsorption isotherms established with an ASAP 2010 sorptometer (Micromeritics) only for the most active samples (with 1, 1.6, and 3% Ni) previously heated at 250°C in air and reduced for 2 h at 400 and 550°C. Dispersion was calculated with the equation proposed by Bartholomew and co-workers (27, 28): $\%D = 1.17 \times V_{ads}\ [\%\mathrm{Ni} \times f]^{-1}$, where V_{ads} is the amount of chemisorbed hydrogen (in mmoles per gram catalyst) and f is the fraction of reduced metal established from O_2 chemisorption measurements carried out at 450°C after running the hydrogen sorption isotherms, assuming the metallic nickel to be completely re-oxidized at that temperature (29). The average metal particle size, d, was obtained using the formula of Coenen and Linsen (30), $d = 431 \times f \times \mathrm{Sm}^{-1}$ in the case of strong metal-support interaction, where Sm, the metal area, was calculated assuming $H/Ni = 1$ and an area of 6.33 $Å^2$ per nickel atom.

Benzene hydrogenation was performed in a continuous-flow microreactor operated at atmospheric pressure. The catalysts were submitted to various activation treatments. Samples were (i) directly reduced with H_2 at 400 and 550°C, (ii) calcined in air at temperatures between 250 and 700°C and reduced at 400 or 550°C, and (iii) heated at 250°C and reduced between 300 and 550°C. In separate runs, the effect of the reduction time (2 and 15 h) was examined. Activation was done in flowing air and/or directly hydrogen (100 ml min^{-1}, ramp of 10°C min^{-1}) for 2 h with, in the former case, an intermediate helium purge prior to the reduction treatment. At the end of the activation, the reactor was cooled at room temperature. Benzene vapor was generated by flowing hydrogen through a glass saturator filled with C_6H_6 (from UCB, highest purity; thiophen content: max: 5×10^{-4}%) and thermostated at 26°C. Hydrogen was purified with Oxy-trap and Hydro-purge (Alltech Associates). The total flow was 20 ml min^{-1} with H_2/C_6H_6 molar ratio of 6.9 (WHSV of 2.7 g C_6H_6 g $cata^{-1}\ h^{-1}$). The reaction was carried out in temperature-programmed mode between room temperature and 350°C at a heating rate of 1.5°C min^{-1}. Similar conditions were adopted in a previous work (31). On-line gas phase analysis of the reaction products was done in a H.P. 5880 gas chromatograph equipped with a thermal conductivity detector and a WCOT Sil-5 capillary column (Chrompack). Cyclohexane was the only reaction product. It was verified that the support alone was totally inactive. The turnovers were established from the H_2 chemisorption data.

RESULTS

Effect of Direct Reduction

Early studies have shown that, in some cases, a more complete reduction to metallic nickel could be achieved when the supported nickel salt was directly reduced with hydrogen rather than when reduction followed a previous calcination in air (29). Samples with 1% Ni dried at room temperature were directly reduced *in situ* at 400 and 550°C. The conversion–temperature curves are compared in Fig. 1 with those obtained over samples previously heated in air at 250°C in order to decompose the precursor and reduced at the two temperatures. At both reduction temperatures, the catalysts treated in air prior to the reduction were more active, thus showing the beneficial effect of a preliminary decomposition of the Ni precursor. It is also clear that the samples reduced at 400°C were more active than those reduced at 550°C, independent of a previous treatment in air.

A duration test has been carried out at 160°C (maximum conversion) for 70 h over a sample with 1% Ni previously

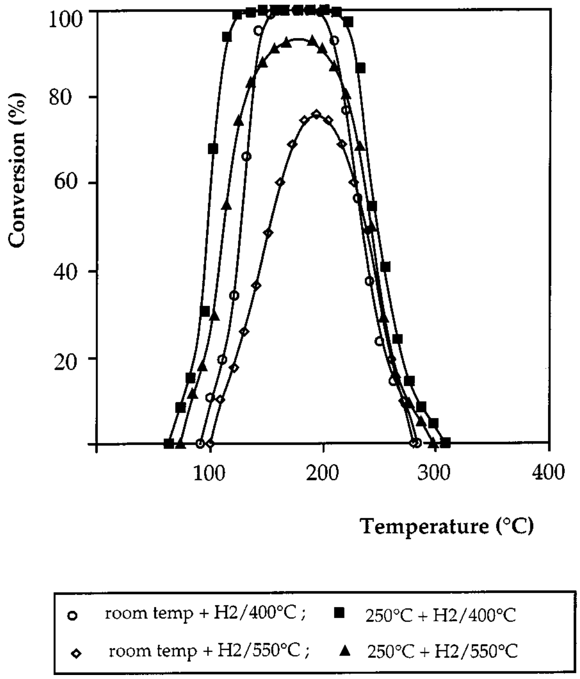

FIG. 1. Comparative conversion vs temperature curves over 1% Ni/Al_2O_3 without and with a previous treatment at 250°C in static air prior to the reduction at 400 and 550°C.

heated at 250°C in air and reduced at 400°C for 2 h. The conversion to cyclohexane was total over the entire period. At the end of the run, the reactor was cooled at room temperature and a temperature-programmed reaction was again performed. The conversion vs temperature curves obtained on the fresh catalyst and after 70 h time on stream are compared in Fig. 2. In both cases, total conversion was achieved, but the plateau of maximum conversion was significantly shortened, indicative of some catalyst deactivation.

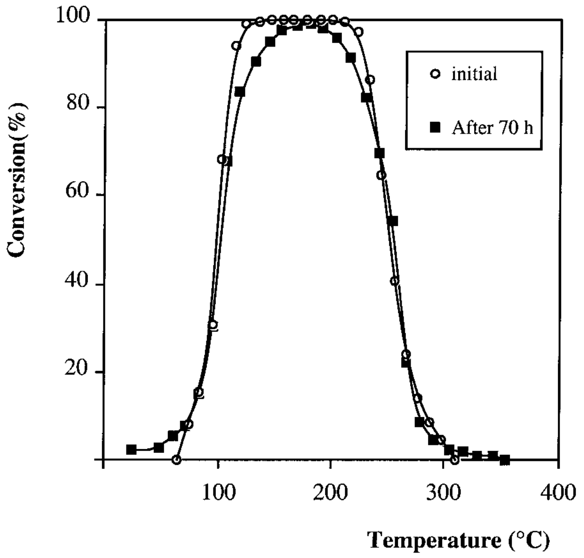

FIG. 2. Conversion–temperature curves over a fresh catalyst and after 70 h of time stream. (sample with 1% Ni).

Effect of Calcination Temperature

Samples with 1% Ni were calcined at temperatures in the 250–700°C range and reduced either at 400 or 550°C, and the conversion–temperature curves are shown in Figs. 3A and 3B, respectively. Clearly, an increase of the calcination temperature depressed the activity, with this effect being more pronounced for the catalysts reduced at 400°C. The catalysts calcined at 700°C prior to the reduction at 400 and 550°C were totally inactive. These observations are consistent with TPR results which showed that increasing calcination temperatures brought about a shift of the temperature

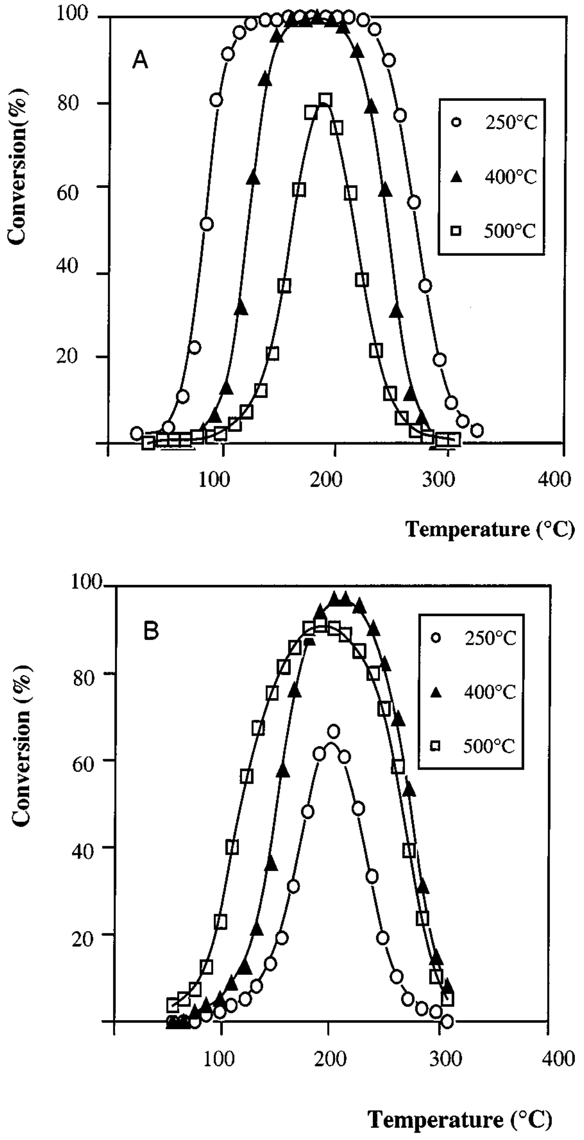

FIG. 3. Influence of calcination temperature (250, 400, 500°C) over 1% Ni/Al_2O_3 reduced at (A) 400°C and (B) 550°C.

of maximum reduction (T_M) of the TPR profile to higher values (25). A sample calcined at 700°C showed, indeed, a T_M value above 900°C. Thus, the inactivity of the samples calcined at 700°C verified that the nickel was not reduced both at 400 and 550°C. For the sample calcined at 500°C, Ni was only partly reduced both at 400 and 550°C (T_M value of 720°C).

Effect of Reduction Temperature and Time

Catalysts with 1% Ni were reduced at temperatures between 350 and 550°C after decomposition of the organic ligands (at 250°C in static air). The conversion–temperature curves are shown in Fig. 4. The samples reduced at 350 and 400°C were more active than those reduced at higher temperature. Reduction at 300°C gave the least active catalyst, probably owing to the smaller fraction of reduced metal. The decreasing activities observed at reduction temperatures above 400°C may partly be accounted for by the poorer dispersion and larger size of the metal particles as inferred from the data of Table 1.

It has been reported that nickel supported on alumina was not completely reduced to the metallic state under typical reducing conditions, but only after several hours of exposure to hydrogen at high temperature (29). Catalysts with 1% Ni heated in air at 250°C were reduced for 2 and 15 h both at 400 and 550°C. As seen in Fig. 5, a prolonged reduction treatment only had a negligible influence on the conversion, with a small loss of activity for the sample reduced for 15 h at 400°C and a slight enhancement of the maximum conversion for the sample reduced at 550°C.

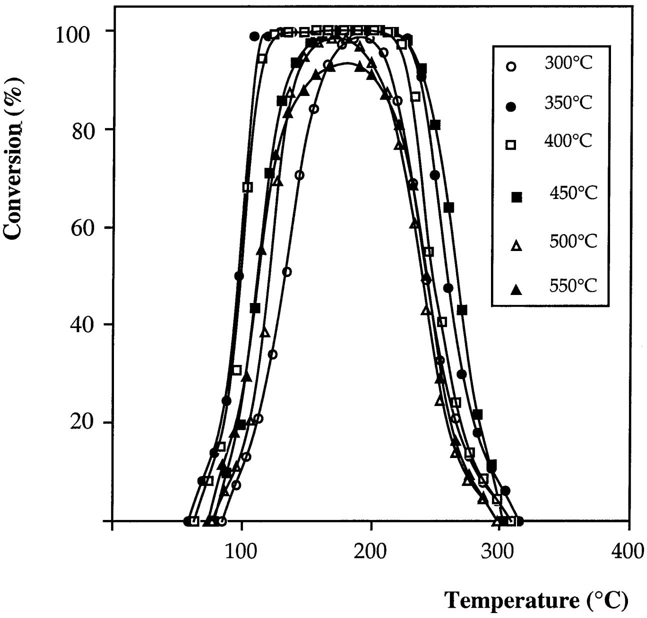

FIG. 4. Influence of reduction temperature over 1% Ni/Al_2O_3 previously heated at 250°C in static air.

TABLE 1

Percentage of Reduced Nickel (*f*, %), Dispersion (D, %), and Average Particle Size (*d*, nm)

wt% Ni (red. *T*, °C)	*f* (%)	*D* (%)	*d* (nm)
1.0–400	26	34	1.9
1.6–400	94	28	2.4
3.0–400	71	18	3.6
1.0–550	71	15	4.3
1.6–550	99	15	4.4
3.0–550	86	8	8.0

Data not collected for 0.4% Ni.

Effect of Nickel Content

Figure 6 shows the variation of benzene conversion vs reaction temperature for catalysts with different nickel contents reduced at (A) 400 and (B) 550°C, respectively, after a previous decomposition of the organic ligands (250°C in air). All the catalysts were active. The maximum conversions and the corresponding temperatures are given in Table 2.

The catalysts with 1 and 1.6% Ni reduced at 400°C were more active than the sample with 3% Ni. The former catalysts achieved total conversion over a wider range of temperatures (plateaus stretching over 87 and 97°C, respectively) than the sample with 3% metal (plateau of 35°C).

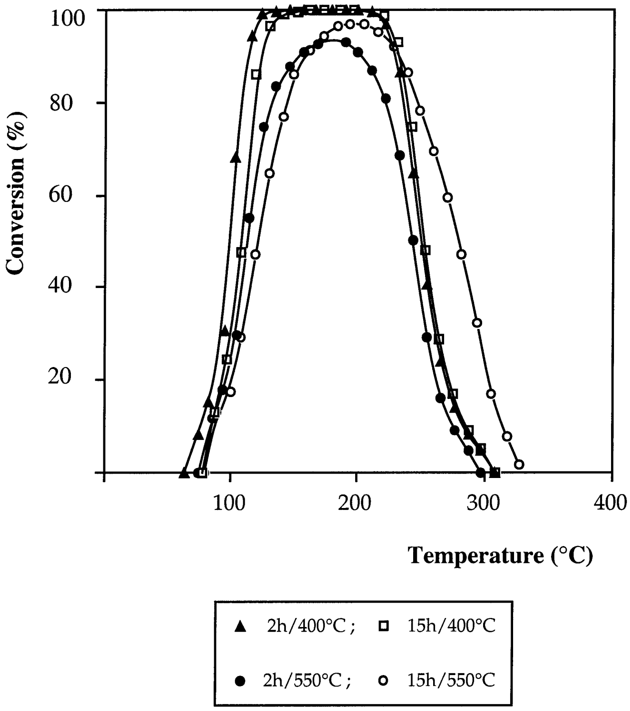

FIG. 5. Influence of reduction time over 1% Ni/Al_2O_3 previously heated at 250°C in static air and reduced at 400 and 550°C.

TABLE 2

Maximum Conversion and Activation Energy

Ni loading (%)-reduction temp. (°C)	Maximum conversion (%)	Temperature at max. conv. (°C)	Ea (kJ mol^{-1})
0.4–400	86	187	62
1.0–400	100	124–211	96
1.6–400	100	125–222	96
3.0–400	100	165–200	80
0.4–550	72	186	60
1.0–550	93	167–190	73
1.6–550	91	179–201	61
3.0–550	100	160–203	79

TABLE 3

TOF (Molecules Benzene s^{-1} $site^{-1}$) at Different Temperatures

Ni (%)-Red. temp. (°C)	75 °C		100 °C	
	Conv. (%)	TOF	Conv. (%)	TOF
1.0–400	9.0	0.052	56.0	0.323
1.6–400	22.4	0.030	87.8	0.119
3.0–400	7.0	0.010	31.5	0.046
1.0–550	1.3	0.006	24.0	0.112
1.6–550	6.8	0.016	22.8	0.054
3.0–550	6.1	0.016	27.5	0.073

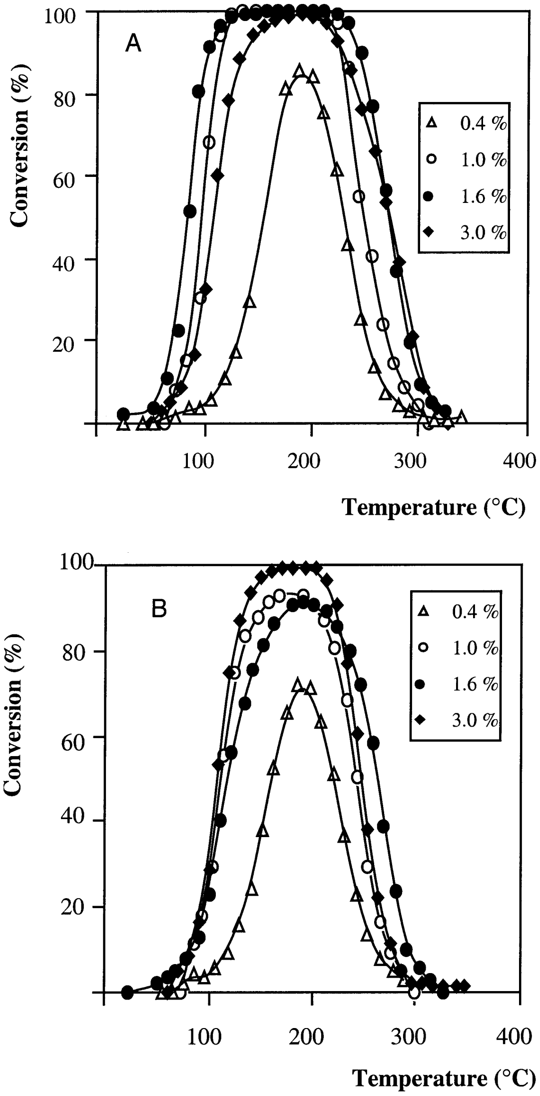

FIG. 6. Conversion–temperature curves over Ni/Al_2O_3 catalysts with different Ni contents previously heated at 250°C in static air and reduced at (A) 400°C and (B) 550°C.

The existence of a plateau at maximum conversion is, of course, related to the experimental conditions (WHSV) in which the catalysts were tested. The larger this plateau, the more active was the catalyst. The catalysts reduced at 550°C were all less active relative to those reduced at 400°C, and the benzene to cyclohexane conversion increased with increasing Ni content. At both reduction temperatures, the catalysts with 3% Ni had similar performances. As seen in Table 1, the more active catalysts exhibited higher metal dispersion and smaller particle size, despite a higher degree of reduction *(f)* at 550 than at 400°C.

The apparent activation energies established from the Arrhenius equation in the temperature 60–160°C range are given in Table 2. They fluctuated between 61 and 96 kJ mol^{-1}, with the highest values for the most active catalysts (1 and 1.6% Ni reduced at 400°C) for which the values leveled off between 100 and 120°C.

Turnover Frequency

The TOF (benzene molecules converted per second and per site) established at 75 and 100°C from the reaction rates and the number of sites determined from the hydrogen chemisorption data are compiled in Table 3. The values at 75°C, namely at low conversions, have been plotted as a function of the particle size in Fig. 7. The TOF decreased for particle sizes between 1.9 and 4 nm (samples reduced at 400°C) and remained nearly constant for the larger particle sizes (samples reduced at 550°C).

DISCUSSION

This study mainly aimed to investigate the hydrogenation efficiency of alumina-supported Ni catalysts with low metal content obtained with nickel acetylacetonate, a precursor so far almost totally ignored for the preparation of such catalysts. The effect of the activation conditions (calcination and reduction temperature) and the relationship between particle size and hydrogenation activity have been examined. Several catalysts reached total benzene conversion at relatively low temperatures with, for some, a plateau at

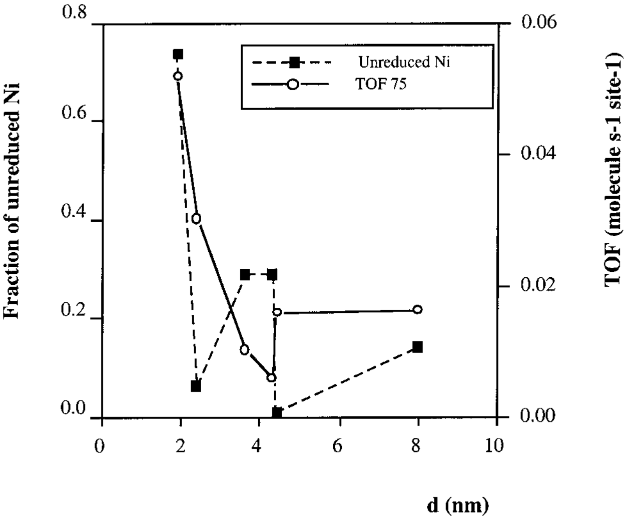

FIG. 7. TOF (at 75°C) and fraction of nonreduced nickel vs particle size for catalysts reduced at 400 and 550°C.

maximum conversion stretching over variable temperature domains. The activity curves showed a positive influence of the reaction kinetics at the lower temperatures, whereas at the higher temperatures, the thermodynamic effect of the reaction was prevailing and the conversion decreased (32). It has been shown that benzene is adsorbed on nickel via π bonding (1), and a reversible maximum for benzene hydrogenation vs reaction temperature has been frequently reported (31, 33, 34) and accounted for by a decrease of the surface coverage by benzene molecules at the higher temperatures (5, 35).

As mentioned earlier, the mechanism of benzene hydrogenation over nickel catalysts still is controversial (18), particularly when hydrogen spillover is involved, as observed in the case of oxide supports (34). Vannice and co-workers (35, 36) proposed an explanation for the effect of the support acidity. According to those authors, the acid sites (in particular the strong Brønsted sites) would act as adsorption centers for benzene molecules, which, in the presence of activated hydrogen, could contribute to the catalyst activity. Protons produced from spillover hydrogen on either strong Lewis or Brønsted sites would activate benzene via the formation of carbonium ions and their hydrogenation to cyclohexane by hydrogen spillover. The alumina support used in this work had only a weak acidity (23), suggesting that if there was a contribution of hydrogen spillover via this mechanism, its participation (if at all) in the overall reaction should be negligible.

It has been observed that submitting the catalysts to a previous heating at 250°C in an oxidizing atmosphere to ensure the decomposition of the *acac* ligands had a beneficial effect on the activity. Under these conditions, removal of the ligands was total (24). This is opposite to the effect of a direct reduction in hydrogen of the metal precursor (generally an inorganic salt), which achieved a higher reduction degree of nickel in Ni/Al_2O_3 catalysts than when reduction was performed after a previous calcination in air (29). The lower activity of catalysts directly reduced under hydrogen suggests that the reduction process could be perturbed by a screening effect of the carbonaceous material around the nickel ion. The decreasing activity of the catalyst treated at temperatures above 250°C probably reflected changes of the metal reducibility, as a result of migrations of Ni^{2+} species to tetrahedral sites of the support where they are stabilized. Consistently, the TPR measurements showed that calcination in air at increasing temperatures was accompanied, at the reduction step, by a shift of the temperature of maximum reduction (T_M) toward higher values, accounted for by the formation of less reducible nickel aluminate-like species (25).

The catalysts reduced at 350 and 400°C were more active than those reduced at higher temperatures. This result is consistent both with the higher metal dispersion and smaller particle size achieved at lower than at higher temperatures (Table 1). A prolonged reduction time (15 h), another parameter quoted earlier in the literature as being important to achieve higher reduction levels (29, 37, 38), did not bring a significant modification of the catalyst efficiency with respect to a reduction period of 2 h (Fig. 5), thus indicating that the degree of reduction of the metal did not significantly change, in line with the stabilization of part of the Ni^{2+} in tetrahedral position of the support.

Catalysts with nickel contents between 0.4 and 3.0% treated in static air at 250°C and reduced for 2 h at 400 and 550°C were all active in this reaction. Those with 1 and 1.6% Ni reduced at 400°C, with higher metal dispersions and smaller average particle sizes, were the most efficient catalysts. It has been estimated that about 2.7 molecules of $Ni(acac)_2$ per nm^2 of the support surface (corresponding to 1.1% Ni) were necessary to ensure a theoretical monolayer coverage (23). When an excess of precursor with respect to that amount is employed (catalyst with 3% Ni,), part of the precursor not directly (or less) interacting with the support surface via a ligand exchange mechanism will probably migrate more easily and be reduced. This could account for the poorer metal dispersion and bigger average particle size and the lower conversion obtained over this catalyst reduced at 400°C relative to those with 1 and 1.6% Ni. For the catalysts reduced at 550°C, in addition to the reduction process, the thermal effect on the migration of Ni species to the tetrahedral and octahedral sites of the support, also existing at lower reduction temperature but to a lesser extent, should also be more pronounced. It has been reported that the nickel distribution between the octahedral and tetrahedral sites in surface $NiAl_2O_4$ strongly depended both on the thermal treatment and nickel loading, the Ni^{2+}_{T}/Ni^{2+}_{Oc} ratio decreasing with increasing nickel content and temperature (39–41). Li *et al.* (41) observed that at low content, nickel preferentially occupied the tetrahedral sites, forming a nonreducible surface spinel, while the enhanced reducibility at higher content was associated to octahedral nickel resembling NiO. These observations may explain the lower activity of the samples reduced at 550°C compared with 400°C. Indeed, the alumina support contained both Al^{VI} and Al^{IV} as found by ^{27}Al MAS–NMR, with a bulk Al^{VI}/Al^{IV} ratio of 4.5/1, whereas the surface ratio established from the XPS Al_{KLL} modified Auger parameters was 1.5/1, thus with a greater relative abundance of Al^{IV} at the surface (24).

The use of the turnover frequencies (TOF) allows one, in principle, to make a valuable comparison with published work, in so far as corrections for differences of the experimental conditions (temperature, concentration, conversion) are made. Since such corrections often are only approximate and sometimes impossible, guidelines to minimize the wide scattering of turnover rates have been proposed (9). TOF data for benzene hydrogenation over supported nickel catalysts compiled by Yoon and Vannice (5) and completed with a few additional results are presented in Table 4. The TOF at 120°C were between 0.014 and 0.160, namely, in the range of the values obtained in this study at 75–100°C, thus showing that the use of Ni(*acac*)$_2$ as a precursor provided very active catalysts, an observation confirmed when comparing with recent literature data. For instance, nickel supported on silica-pillared zirconium-titanium phosphates (Ni/SPP in Table 4) with metal contents between 8 and 15% had TOF values at 170°C (14) in the range of 0.046–0.093 (at conversions between 12 and 47%), i.e., similar to those obtained in this study at 75–100°C. Values reported by Marécot *et al.* (18) at 50°C were an order of magnitude lower than those obtained at 75°C with our catalysts. The TOF values obtained at 140°C over catalysts with 6 to 10% Ni supported on Al_2O_3, SiO_2, TiO_2, ZrO_2, and MgO (42) were of the same order of magnitude as those obtained in this work at 75–100°C. Ni–US–Y zeolites with Ni contents between 0.76 and 2.25% were nearly inactive between 100 and 150°C (6), while Ni/fluorinated alumina-pillared α-zirconium phosphate with less than 10% Ni were weakly active (43). Also, early studies showed that Ni/Al_2O_3 catalysts with less than 3% Ni were virtually inactive in this reaction (44). Finally, Ni/Al_2O_3 catalysts prepared by vapor-phase deposition of nickel acetylacetonate were inactive in toluene hydrogenation for nickel contents below 5% (45, 46). Under the experimental conditions used in this work, the catalysts with only 1% Ni exhibited a relatively high catalytic activity and fair stability.

TABLE 4

Turnover Frequencies (TOF) and Apparent Activation Energies (Ea) from the Literature

Catalyst	TOF (molec. Bz s^{-1} $site^{-1}$)	Ea (kJ mol^{-1})	Ref.
25% Ni/Al_2O_3	0.014	42.2	(5)
67% Ni/kieselguhr	0.028	50.2	(5)
10% Ni/SiO_2	0.058	58.5	(5)
10% Ni/SiO_2	0.066	58.5	(5)
4 to 60% Ni/SiO_2	0.080	79.0	(5)
Ni/SiO_2,Al_2O_3	0.110	58.5	(5)
11.3% Ni/SiO_2	0.160	52.2	(5)
6 to 10% Ni/VS	0.010–0.100	—	(38)
2 to 20% Ni/SiO_2	0.004–0.029	50.6–56.4	(18)
23% Ni/Al_2O_3	0.002	—	(18)
8 to 15% Ni/SPP	0.045–0.093	—	(14)

Note. (5), TOF adjusted at 120°C; (38), TOF at 140°C with various supports (VS); (18), TOF at 50°C; (14), TOF at 170°C for silica-pillared Zr–Ti phosphate (SPP).

As mentioned in the Introduction, gas-phase hydrogenation of benzene was initially considered as structure insensitive on metals (11–13), but divergences appeared in the case of nickel catalysts (6, 11–15, 17–19, 38, 47) illustrating, in agreement with Che and Bennett (10), that generalization may be risky. This reaction was shown to be structure insensitive at high reaction temperatures, while structure sensitivity is most frequently admitted at low temperatures (38, 47). However, "low" and "high" temperatures are relative as it appears from different studies. Indeed, structure sensitivity in the case of supported nickel catalysts was observed at 25 (19), 50 (18), 70 (47), 100 (6), and 170°C (14). In addition, the TOF values obtained at 120°C by different authors varied by an order of magnitude (Table 3), suggesting that structure sensitivity at this temperature could be assumed. A similar remark was made in the case of supported Pt catalysts (35). At the opposite, structure insensitivity was concluded at 170 (40), 210 (48), and between 100 and 200°C (49). Martin and Dalmon (16) showed that the reaction was sensitive at low temperature (30°C), and became less structure sensitive at high temperature (327°C). For Aguinaga *et al.* (50), the scattering of the data obtained at 200°C did not permit to conclude on an effect of the average nickel particle size.

The results of this study (Tables 1 and 3 and Fig. 7) showed a decrease of the TOF when the metal particle size increased, suggesting that the reaction is structure sensitive for nickel particles smaller than about 3–4 nm (reduction temperature of 400°C) and insensitive for particles above this size (reduction temperature of 550°C). According to Coenen *et al.* (19), the specific activity vs crystallite size should not vary by a factor greater than three for a facile reaction. The difference of sensitivity is clearer when considering the TOFmax/TOFmin ratio obtained at a given temperature and for catalysts prepared by the same method. For the two temperatures chosen (75 and 100°C), a factor between 5 and 7 was observed for the samples reduced at 400°C and between 1.5 and 2.7 for those reduced at 550°C.

A similar behavior as a function of reduction temperature was observed for supported nickel catalysts (16, 47, 50, 51).

In the case of Pt/Al_2O_3 catalysts, benzene hydrogenation at 80°C was structure sensitive at reduction temperatures in the 100–300°C range and insensitive at reduction temperatures of 400°C and above (52). Surprisingly, Aguinaga *et al.* (50) obtained smaller nickel particles in catalysts reduced at 500 relative to 300°C. They also observed two different behaviors but no interpretation was proposed. Martin and Dalmon (16) showed that when NiO was reduced at temperatures lower than 500°C, the activity did not vary much with the particle size, while above 500°C, the activity decreased as particle size increased. The authors concluded that the activity did not depend unequivocally on the size of the metal particles. This apparent contradiction with the present results is probably due to the fact that our catalysts were all supported, while the results of the cited authors were obtained on bulk nickel catalysts.

Anderson *et al.* (47, 51) reported that the TOF was influenced both by the degree of reduction and the particle size, and they proposed that the apparent structure sensitivity was the result of the presence of unreduced Ni at the support surface, the role of which is interpreted as reducing the size of the nickel particles required for the adsorption of benzene in a planar mode (51). In order to verify this effect, plots of the fraction of unreduced Ni vs particle size were established from the experimental values obtained at 75°C (Fig. 7). A similar variation was obtained with the values established at 100°C. The trend of Fig. 7 was qualitatively similar to that of the cited authors. The slight differences noticed are probably related to the fact that these authors took into account the unreduced Ni determined by XPS, while in this work, it was deduced from the O_2 chemisorption data determined at 450°C. This figure verifies the proposition of those authors that unreduced Ni also has an influence on the activity.

CONCLUSION

Ni/Al_2O_3 catalysts with low Ni contents prepared with nickel acetylacetonate exhibited high hydrogenation activity provided that the organic ligands were previously decomposed in air at moderate temperature (250°C). Higher decomposition temperatures depressed the catalyst efficiency, as a result of a partial formation of nickel aluminate. Different results were obtained according to reduction temperature. Catalysts reduced at 400°C, with smaller Ni particle sizes and higher dispersions, were more active than those reduced at 550°C. From the variation of the TOF with metal particle size, the reaction appeared to be structure sensitive for particles smaller than 4 nm and insensitive for bigger particles. The catalytic activity was also influenced by the amount of nonreduced nickel. Higher catalytic efficiency was concluded from the comparison of the TOF values obtained for catalysts prepared from Ni-acetylacetonate with those reported in literature for similar catalysts prepared with inorganic precursors.

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