

Nanosized Bimetallic Ni-Sn and Ni-Zr Catalysts Prepared by SOMC/M route. Characterization and Catalytic Properties in Styrene Selective Hydrogenation

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In this article, we will present the synthesis of bimetallic Ni-based catalysts aiming to perform selective hydrogenation. First a parent catalyst constituted of small nickel particles supported on silica with very narrow size distribution around 3.5 nm, has been prepared. Then controlled modification by site, using the SOMC/M route described by Candy *et al.* 1994 and organometallic compounds of Sn and Zr, allows to explore both the geometric and electronic effects in the selective hydrogenation of styrene into ethylbenzene.

1. Introduction

Products coming from refining process of crude oil contain diolefinic and alkenylaromatic compounds which can easily polymerized to produce gums that could deactivated catalysts and plug reactors used in following steps. Hydrogenation of these double bonds inhibits this process, but, following Le Page 1978 and Chauvel *et al.* 1985, total hydrogenation could induce both a dramatic increase of the reaction temperature and a severe lost of octane number of the fuel.

According to Lumbroso 1979, sulfur modified nickel catalysts supported on alumina are used to selectively hydrogenate diolefins into olefins and styrenic derivatives into alkylaromatics. Sulfur compounds such as dimethylsulfur or thiophene are used to modify the surface of nickel particles. It is generally proposed that about one sulfur atom for four surface nickel atoms is needed to inhibit the hydrogenation of the aromatic rings while diolefins and styrenics are only partially hydrogenated. However sulfur deposition is not so easy to control at industrial scale. Insufficient passivation by sulfur leads to dramatic increase of the reactor temperature while too much passivation leads to formation of Ni₃S₂ which is completely inactive.

It is generally accepted that the observed selectivity in the hydrogenation of carbon-carbon double bond against aromatic ring could be due to geometric effect of sulfur. But, since sulfur is clearly more electronegative than nickel ($\chi=2.5$ against 1.8 for Ni) in the Pauling classification, an electronic effect cannot be rejected.

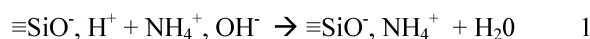
The aim of the present work was therefore to replace sulfur by another compound either equivalent (Sn) or less (Zr) electronegative than nickel in order to explore the possible electronic and/or geometric effects in selective hydrogenation. First a parent catalyst constituted of small nickel particles supported on silica with very narrow size distribution around 3.5 nm, has been prepared. Then modified nickel catalyst has been prepared by controlled modification by site, using the SOMC/M route described by Candy *et al.* 1994 and organometallic compounds of Sn and Zr.

Styrene presents both an olefinic double bond and an aromatic ring. Thus, hydrogenation of styrene first into ethylbenzene and then into ethylcyclohexane could be a good test reaction. It is generally observed that hydrogenation of styrene into ethylbenzene proceeds with an activation energy of about 20 kcal/mol, as reported by Zhou *et al.* 2007 while the one of benzene hydrogenation is close to 50 kcal/mol, according to Anderson *et al.* 1994. Moreover, at temperature around 100°C, the hydrogenation of styrene into ethylbenzene is more than hundred times faster than the hydrogenation of ethylbenzene into ethylcyclohexane. Thus, a particular procedure for the hydrogenation of styrene has been used in order to easily compare the kinetics of the two reactions in one experiment.

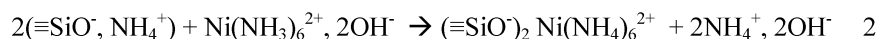
2. Experimental

2.1 Preparation of parent Ni/SiO₂ catalyst

Ni/SiO₂ parent catalyst was prepared by the ion exchange procedure describe by Bonneviot *et al.* 1989, using hexamine nickel hydroxide. In a first step, the acidic protons of the silica surface are exchanged by NH₄⁺ groups, in ammonia solution at pH 9 as described in equation 1.



Then, the hexamine nickel hydroxide is added to the aqueous suspension at pH 9 (*cf* equation 2) and the system was slowly stirred during about 10 hours.



The obtained solid is filtered and washed with distilled water and then dried under vacuum before decomposed under flowing hydrogen at increasing temperature from 25 to 600°C in 5 hours into a quartz tubular reactor. The temperature is then decreased to room temperature and hydrogen is replaced by nitrogen. The sample is kept under air.

2.2 Characterization of the catalysts

Transmission Electron Microscopy experiments are performed at IFP-Lyon using a JEOL 2100F apparatus operating at an acceleration voltage of 200 kV.

Magnetic measurements are performed at room temperature, using a IRCELyon home made magnetometer according to the extraction method of Selwood 1976. The magnetic field varies from 0 to 2 Tesla. Before measurements, the samples are reduced under hydrogen at 500°C during 3 hours and then evacuated under vacuum at 350°C to remove adsorbed hydrogen.

Volumetric measurements are performed in a static mode using a home made C2P2 adsorption apparatus already described by Candy *et al.* 1988.

These techniques allow to determine the dispersion (D) of the nickel particles (amount of surface nickel atoms divided by the total number of nickel atoms, $D = \text{Ni}_s/\text{Ni}$).

2.3. *In situ* modification of the parent catalyst

Before reaction, 20 mg of Ni/SiO₂ catalyst are reduced under flowing hydrogen at 500°C during 3 h. Then, after cooling to room temperature they are transferred without contact with air, into the autoclave, in suspension in the n-heptane solvent. For modification of the parent catalyst, tin is added on the reduced nickel catalyst surface by grafting of tetrabutyltin (SnBu₄) in the autoclave, in n-heptane solution, at 130°C, under 30 bars of hydrogen pressure. Zirconium is added to the nickel catalyst by reaction of bis-cyclopentadienyldimethylzirconium (ZrCp₂Me₂) in the same manner as for tin.

Styrene (Styrene/Ni_s=3100) and dodecane as internal standard are then introduced into the autoclave at 40°C under 30 bars of hydrogen and styrene hydrogenation begins.

2.4 Styrene hydrogenation reaction

Styrene hydrogenation was conducted in a well stirred stainless steel autoclave (Parr Instrument, 100 mL of capacity, magnetically drive stirrer). The reaction is followed by gas chromatography analysis of samples taken at regular interval of time.

Since the reaction rate of styrene hydrogenation into ethylbenzene is more than 100 times faster than the reaction rate of ethylbenzene hydrogenation into ethylcyclohexane, the reaction was conducted in two steps. In the first step, the temperature is constant at 40°C under 30 bars of hydrogen and 700 rp/min until the styrene is transformed into ethylbenzene. Then, the temperature is raised to 130°C under lower pressure and stirring speed. In the second step, the temperature is maintained at 130°C under 30 bars of hydrogen and 700 rp/min to transform ethylbenzene into ethylcyclohexane. An example of reaction is given in Figure 1.

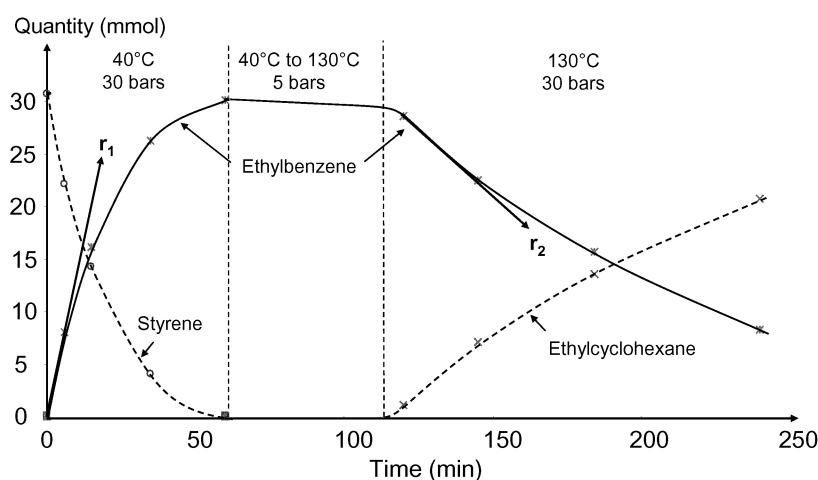


Figure 1. Styrene hydrogenation, 50 mL n-heptane, 20 mg of catalyst, Molar ratio styrene/Ni_s=3100, First step, temperature 40°C, hydrogen pressure 30 bars, 700 rp/min for 1 h, then 40°C to 130°C under 5 bars and 50 rp/min for 1h and second step 130°C, 30 bars, 700 rp/min.

For each step, the initial reaction rates (r_1 and r_2 , see Figure 1) are calculated from the slope of the ethylbenzene consumption in function of time at the beginning of the two steps (see figure 1). The results are reported to the $(r_1)_0$ and $(r_2)_0$ rates measured in the same conditions with Ni/SiO₂ parent catalyst, to obtain $(r_1)_n = r_1/(r_1)_0$ and $(r_2)_n = r_2/(r_2)_0$. The selectivity of the modified catalysts can be expressed as $S = (r_1)_n / (r_2)_n$.

3. Results and discussion

3.1 Silica supported nickel catalyst

Silica support is Aerosil 200 from Degussa with a specific surface area of 200 m²/g.

The nickel loading is 11 % weight, as determined by elemental analysis.

TEM picture acquired in dark field mode (Figure 2) show metallic particles randomly distributed on the support surface, with a pretty narrow particles size distribution and a mean diameter in volume distribution of 3.1 nm.

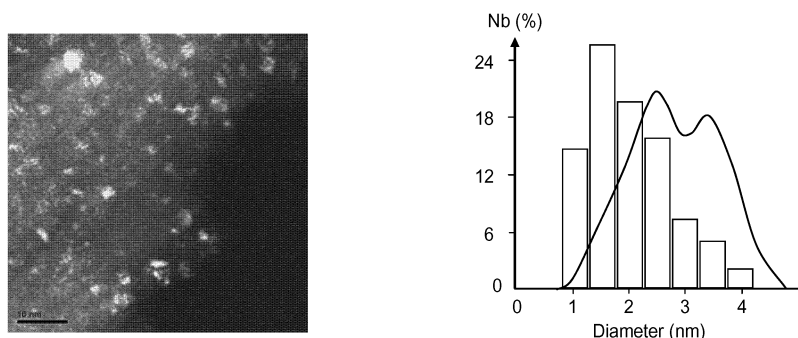


Figure 2. TEM picture of Ni/SiO₂ catalyst and particle size distribution in number (histogram) or in volume (line).

After reduction under flowing hydrogen (50 mL/min/g) at 600°C during 4h and treatment under vacuum (10⁻⁶ mbar) at 350°C during 3 h, the magnetic isotherm obtained is reported in figure 3.

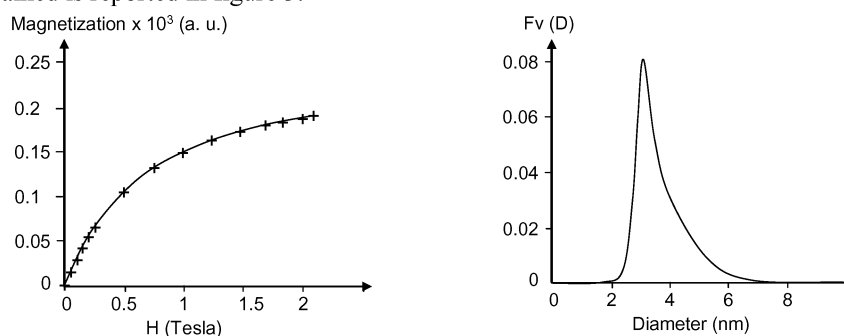


Figure 3. Magnetic isotherm of Ni/SiO₂ catalyst and particles size distribution according to software developed by S. Adjimi, K. Fiaty and J-A. Dalmon. LAGEP - IRCELYon - IFPLyon.

From the magnetic isotherm, we can deduce the reduction rate of 95.8% and a narrow size distribution with a mean diameter of 3.9 nm.

After reduction under flowing hydrogen at 600°C during 4h and treatment under vacuum (10⁻⁶ mbar) at 350°C during 3 h, hydrogen chemisorption isotherm (25°C) reported on figure 4 gives a dispersion (D) of the catalyst of 29%, assuming that one surface nickel atom chemisorbed one hydrogen atom (H/Ni_s=1). Assuming a cubooctahedral shape for the metallic particles (Figure 4), this dispersion corresponds to particles size of 3.4 nm.

There is a very good accordance between the three methods. The slightly smaller particles size (3.1 nm) obtained by TEM in the dark field mode can be explained because only monocrystallin domains are observed by this technique.

From this study, it can be concluded that silica supported nickel particles (11% weight loading), randomly distributed on the silica surface with a narrow size distribution where prepared. From TEM, volumetric and magnetic measurements, an average mean diameter around 3.5 nm was determined. These particles were fully reduced by treatment at 600°C under flowing hydrogen.

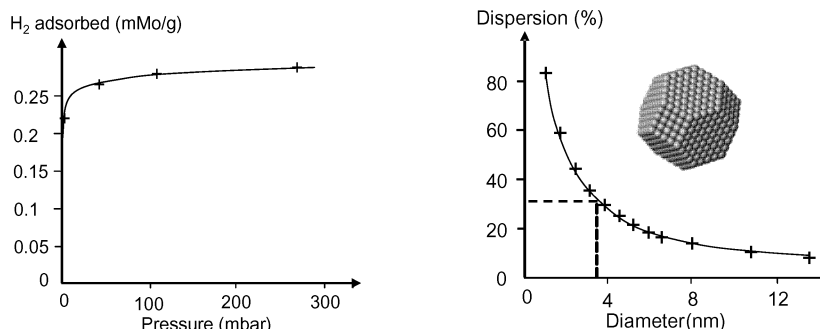


Figure 4. Isotherm adsorption of hydrogen, 25°C on Ni/SiO₂, relation between dispersion and particle diameter.

3.2. Styrene hydrogenation with NiSn/SiO₂ and NiZr/SiO₂ catalysts

The results obtained with Sn and Zr modified Ni catalysts are reported on Table 1 and in Figure 5. In the case of Sn, various ratio Sn/Ni_s were investigated.

Table 1. Influence of Sn and Zr on the reaction rate for styrene hydrogenation into ethylbenzene (r_1) or ethylcyclohexane (r_2) and respective selectivities (S).

Doping metal M	M/Ni _s	(r_1) _n = $r_1/(r_1)_0$	(r_2) _n = $r_2/(r_2)_0$	$S=(r_1)_n/(r_2)_n$
Sn	0.05	1.5	0.8	1.8
Sn	0.2	0.85	0.65	1.3
Sn	0.5	0.3	0.6	0.5
Zr	0.3	1.1	0.8	1.4

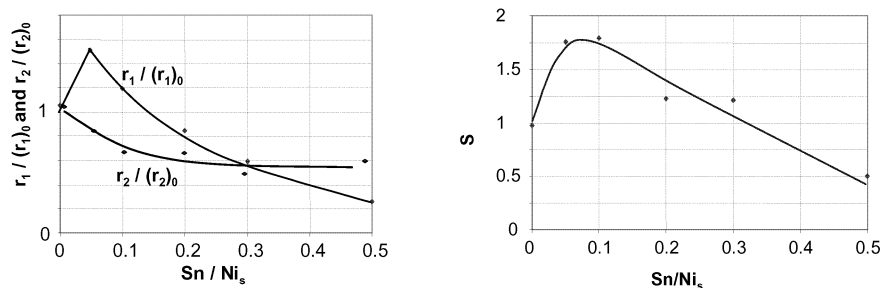


Figure 5. Styrene hydrogenation on NiSn_x/SiO₂, (conditions described in Figure 1).

For amounts of SnBu₄ introduced corresponding to Sn/Ni_s values lower than ca. 0.7, the SnBu₄ introduced reacts on the catalyst surface with total hydrogenolysis of the Sn-C4 bonds and formation of naked tin atoms deposited on the nickel surface, as previously demonstrated by Lesage et al. 1995. For very low tin content, between 0 and 0.05 Sn/Ni_s, there is an increase of the styrene to ethylbenzene reaction rate (r_1) and a decrease of the ethylbenzene to ethylcyclohexane reaction rate (r_2) as compared to pure nickel catalyst. For Sn/Ni_s=0.2, the hydrogenation rate of the double bond is the same as pure nickel while the reaction rate of the aromatic ring is lower. Above this value, both

the reaction rates are lower on doped catalysts. The results obtained indicate a possible optimum of selectivity for ca 0.1 Sn/Ni_s (S=1.8).

Clearly, the tin addition has a weak effect on the selectivity of the NiSn/SiO₂ catalysts for the styrene hydrogenation into ethylbenzene. Since electronegativity of tin is the same as the one of nickel, an electronic effect is not effective, and it is shown that the simple geometric effect is not enough to reach high selectivity.

For Zr/Ni_s value of 0.5, there is a slight increase of the hydrogenation rate of styrene to ethylbenzene, $r_1/(r_1)_0=1.1$ and a slight decrease of the hydrogenation rate of ethylbenzene to ethylcyclohexane, $r_2/(r_2)_0=0.7$. Although the electronegativity of Zr is largely greater than Ni, the addition of Zr from ZrCp₂Me₂ on the nickel catalyst does not clearly increase the selectivity of the styrene hydrogenation into ethylbenzene as compared to Sn addition. Note that since Zr is added *in situ* at low temperature, it is expected that there is no alloy formation, and that Zr atoms are located on the surface of the nickel nanoparticles.

4. Conclusion

Silica supported nickel catalyst with 11 % weight loading and a narrow size distribution around 3.5 nm was prepared.

This parent catalyst was doped with Sn or Zr, using organometallic precursors.

Bimetallic catalysts were tested in the hydrogenation of styrene into ethylbenzene and ethylcyclohexane.

A slight increase in selectivity for ethylbenzene hydrogenation was observed for Sn and Zr doped samples. Since Sn and Zr have very different electronegativities, the geometric effect seems to be predominant in the case of nickel surface modification.

5. References

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