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Research Article

Hydrogenation of Tetralin over Supported Ni and Ir Catalysts

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Selective hydrogenation and ring opening (SRO) of tetrahydronaphthalene (tetralin) was studied over nickel and iridium supported catalysts in the context of the removal of polynuclear aromatics from diesel fuel. The tetralin hydrogenation was carried out in a fixed-bed reactor at 270°C, using H_2 pressure of 30 bars, WHSV of 2.3 h^{-1}, and H_2/feed molar ratio of 40; the resultant products were analyzed by GC and GC-MS. The Ir/SiO_2 catalyst gave 85% of tetralin conversion and 75.1% of decalin products selectivity whereas Ni/SiO_2 catalyst showed an unprecedented high catalytic performance with 88.3% of tetralin conversion and 93% of decalin products selectivity. The catalysts were characterized by using different characterization techniques such as XRD, TPR, and HR-TEM to know the physicochemical properties as well as active sites in the catalysts.

1. Introduction

At current stage, the demand for clean and high-quality transportation fuels is increasing, and environmental regulation of their specifications is becoming more stringent [1]. These developments pose not only economic but also technological challenges for the global refining industry. Light cycle oil (LCO) is a side product of the fractionation of fuel catalytic cracking (FCC) unit. The characteristics of LCO are within the diesel fuel range, but it is a poor diesel fuel blending component due to high sulfur and nitrogen content, high content of aromatic componds, high density, and low cetane number (CN). High percentage of aromatic compunds not only generate emissions of undesired particles in exhaust gases but also decrease the CNs [2]. Due to stringent environmental regulations and fuel specifications, reduction of aromatic compunds in distillate fuels is a topic of enormous interest in petroleum/automotive industries research worldwide [2]. Hydrogenation of aromatic compounds is important for the production of high performance diesel fuel (low aromatic diesel fuels) [1–4]. It has been reported in the literature that the aromatic compounds present in LCO are mostly the diaromatics (naphthalenes) compounds [5]. The hydrogenation of these diaromatics in fuels into monoaromatics is easy, but their complete saturation is more difficult due to reversibility of hydrogenation reaction [5, 6]; hence in the hydrogenation and SRO studies, tetralin and naphthalene have been often considered as model molecules representative of diesel fuels [5–8].

From the hydrogenation of tetralin, one can obtain either *trans*- or *cis*-decalin depending on the structure of intermediate located on the surface [9]. Even though, these two isomers have similar physical properties, they are associated with different chemical properties and different thermal stability [10, 11].

Cyclic saturated hydrocarbons such as decalin, bicyclohexane, methylcyclohexane, and are proposed as new mobile hydrogen storage media for proton exchang membrane fuel cells. Hydrogen can be obtained by catalytic dehydrogenation of the cyclic saturated hydrocarbons to corresponding aromatic compounds and stored by the hydrogenation of the aromatic products. As per literature [12], *cis*-isomer is more preferable for hydrogen production, because dehydrogenation rate of *cis*-decalin is faster than that of *trans*-decalin [12]; *cis*-decalin can also be used to produce sebacic acid that is used in the manufacture of 6,10-Nylon and softeners [13]. Song et al. demonstrated that, *trans*-decalin is superior as compared to *cis*-decalin for jet fuel components, due its high temperature stability as compared with *cis*-decalin [10]. It could be worthwhile to mention that SRO is the promising process for the improvement of diesel quality and CN. Decalin is not the final products of tetralin SRO, but it is one of the most desired intermediate, specially *cis*-decalin from which we obtained high selectivity for the ring opening/contraction (ROCP) products. After considering the wide application of decalin [9–12] in various fields, the hydrogenation of tetralin to decalin is an industrially important reaction.

Noble metal catalysts like Ir, Pt, Pd, and Ru are predominantly used for the hydrogenation of aromatics compounds and selective ring opening process [14–17]. Due to their cost effectiveness and prone to the sulfur poisoning, it has been necessary to develop a less expensive but efficient catalyst for the hydrogenation process. The impregnation method is one of the most widely adopted methods to prepare a metal-supported catalyst on a high surface area material [18]. In our previous studies, we observed that Ni/SiO_2 catalyst offers appreciable RO selectivity from MCH [19] and MCP [20] as compared with reported noble metal catalysts [18]. In present study, we have compared the catalytic activity of Ni/SiO_2 catalyst with noble metal containing Ir/SiO_2 catalyst for the hydrogenation of tetralin. The influence of different supports (Ir/SiO_2, Ir/ASA, and Ir/USY) on the hydrogenation and ROCP selectivity during tetralin hydroconversion was also studied.

2. Experimental

2.1. Catalyst Preparation. All the Ir supported catalysts were prepared by impregnation method. The support materials SiO_2 (Junsei Chemical Company Ltd, Japan), USY zeolite (Si/Al = 40, Zeolyst International, USA), and amorphous silica-alumina (ASA) (Si/Al = 40, Sasol) were used as received. The Ir catalyst with 0.9 wt.% loadings was impregnated on support using aqueous solutions of $IrCl_3{\cdot}3H_2O$ (Samchun Pure Chemicals Ltd, Korea). After impregnation, the catalysts were dried overnight in the oven at 100°C and then calcined at 400°C for 4 h in air [17, 18]. The Ni/SiO_2 catalyst with 60 wt.% of Ni loading was prepared by coprecipitation method, using the desired amount of nickel precursor $Ni(NO_3)_2{\cdot}6H_2O$, and $Na_2SiO_3{\cdot}H_2O$ as silica source and urea as a precipitating agent. Precipitation was done at 90°C with constant stirring and maintained the final pH of 8 to 8.5. The resultant solution was stirred for 24 h, followed by aging for 10 h. Finally, the resultant green precipitate was collected after filtration and washing. The sample was dried in an oven at 110°C for 6 h and calcined at 500°C for 5 h. Details of preparation procedure and characterizations were reported in the previous report [19, 20].

2.2. Catalyst Characterization. Temperature programmed reduction (H_2-TPR) was used to examine the metal/support interaction and to find out the reduction temperature of catalysts. H_2-TPR experiment was carried out in a Micrometrics 2920 AutoChem II chemisorption analyzer, equipped with thermal conductivity detector (TCD). 0.2 g of catalyst was placed in sample holder and pretreated at the 100°C for 2 h. TPR was performed in the temperature range of 50°C to 800°C with a heating rate of 10°C/min. The H_2 consumption was monitored by a TCD.

BET surface area, pore size, and pore volume measurements of the catalysts were determined from a physical adsorption of N_2 using liquid nitrogen by an ASAP2420 Micromeritics adsorption analyzer (Micromeritics Instruments Inc). All the samples were degassed at the 250°C for 2 h prior to the measurements to remove the adsorbed moisture from catalysts surface and pores. The surface area and pore size distribution (PSD) were calculated from the BET and BJH equations, respectively, by the instrument software.

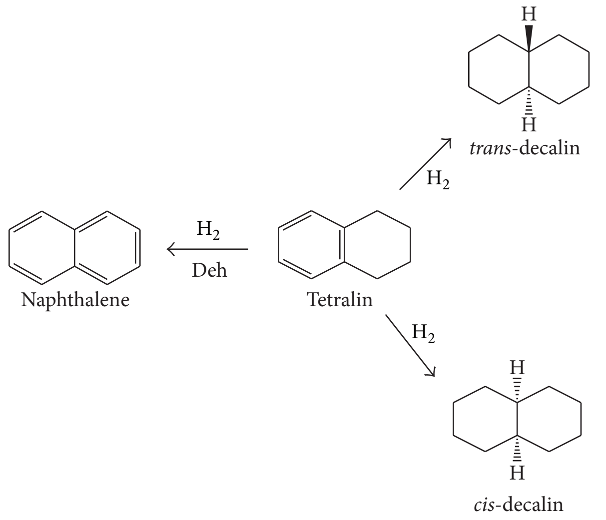
Powder X-ray diffraction patterns were recorded on a Rigaku D/Max-3c diffractometer, equipped with graphite monochromator and operated at 40 kV and 40 mA (Cu-K_α radiation); the average crystallite size was calculated using the Scherrer equation. The morphology and metallic dispersion of catalyst were determined by transmission electron microscope (TEM) on JEOL JEM-2010.

2.3. Catalyst Activity Measurement. The hydrogenation of tetralin was performed in a fixed-bed reactor at a temperature of 270°C, H_2 pressure of 30 bars, WHSV of $2.3\,h^{-1}$, and H_2/feed molar ratio of 40. In a typical experiment, the catalysts were palletized, crushed, and sieved to 500 mesh size; about 0.5 g of catalyst was loaded in the reactor. Prior to the reaction, the Ni-catalyst was reduced in situ with (5%) H_2 flow at 330°C, and Ir-catalyst at 210°C after which the reactor was adjusted at operating conditions. The optimum temperature for reduction of catalysts was determined based on the H_2-TPR analysis. The liquid products were collected and analyzed by a GC (DS Chrome 6200, Donam Instruments Inc, Korea) equipped with an FID detector and DB-1HT fused capillary column (Alltech, USA) (30 m × 0.2 mm × 0.5 μm), using helium as a carrier gas. Identification of GC peaks was accomplished by GC-MS analysis by Agilent HP 5973 GC-mass spectrometer.

Schematic representation of products obtained from the hydrogenation of tetralin is shown in Scheme 1. *cis*- and *trans*-decalin are the hydrogenation products which further gived ROCP and cracking (CR) products by hydrogenolysis of endocyclic C–C bond of decalin (ROCP and CR products are not shown in Scheme 1).

3. Results and Discussion

3.1. Catalysts Characterization. H_2-TPR was conducted to know the reduction temperature of Ni and Ir on SiO_2. Figure 1 represents the TPR analysis of catalysts. The Ni catalyst showed the reduction peak at 330°C, which is at higher reduction temperatures than the corresponding Ir catalysts at 210°C. Hence, prior to the hydrogenation reaction in fixed bed, catalyst was reduced at the reduction temperatures obtained from TPR analysis for each metal catalyst. In TPR profile of both the catalysts, the metallic reduction peak appear at lower reduction temperature which is due to its higher dispersion on the support [17, 20]; the higher metallic



Scheme 1: Products obtained from the hydrogenation of tetralin (Deh—dehydrogenation).

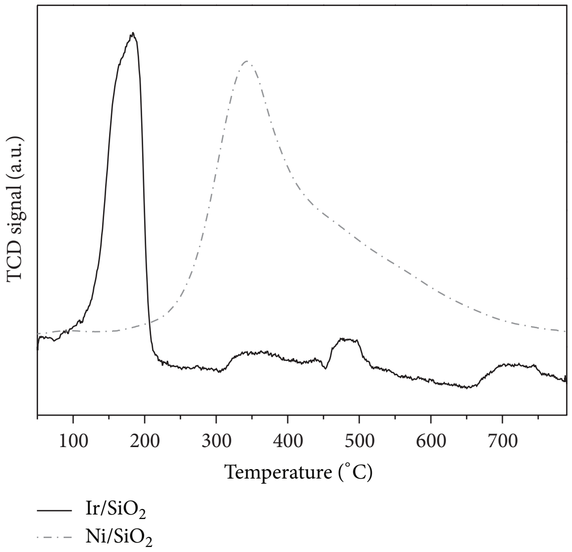


Figure 1: H_2-TPR profiles of fresh Ni/SiO$_2$ and Ir/SiO$_2$ catalysts.

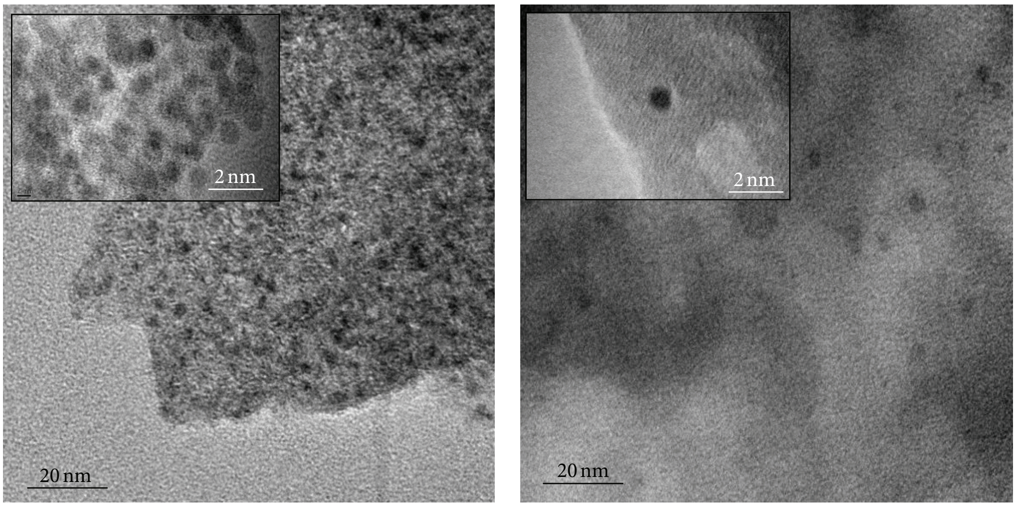
dispersion could allow access to hydrogen for easy reduction of supported metallic particles.

In XRD pattern (not shown here) of Ir/SiO$_2$ catalysts, we could not observes any crystalline phase related to the iridiumes and it is mainly due to high dispersion of Ir nanoparticles as well as due to the low loading of metal (0.9 wt%). For Ni/SiO$_2$ catalyst, detailed characterization is given in previous reports [19, 20]. The result of XRD analysis, concerning highly dispersed nickel particles with a small particle size (2-3 nm), was also conformed through the HR-TEM analysis. The XRD pattern of both the catalysts was found to be the same after reaction.

The HR-TEM micrographs of reduced Ni/SiO$_2$ and Ir/SiO$_2$ catalysts are shown in Figure 2. By the thorough examination of the TEM images of both catalysts, both catalysts possessed high dispersion of metallic Ni and Ir, having an average particle size of around 2-3 nm. The higher dispersion of metallic nanoparticles on the supports allows their low temperature reduction, and hence the higher hydrogenation activity was observed at moderate reaction conditions. The morphology of each catalyst was also checked after hydrogenation reaction through TEM analysis, and it was also confirmed through the XRD analysis, it was found to be the same as fresh one. It means; both the catalysts can be allow their reusability for the next run. The BET surface areas for both the catalysts before and after reaction was also evaluated through N_2 adsorption study and after the reduction the surface areas found to be 176 m^2/g for Ni/SiO$_2$ and 172 m^2/g for Ir/SiO$_2$. It could be very interesting to know that the surface area of both the used catalysts were obtained very similar to fresh catalysts.

3.2. Hydrogenation and Selective Ring Opening of Tetralin. In both catalysts, *cis*- and *trans*-decalins were obtained as major products from tetralin hydrogenation, along with the other hydrogenation products such as ROCP and CR, and it could be clearly seen on the GC chromatogram (Figure 3), but naphthalene was not obtained under these reaction conditions (at 270°C, using H_2 pressure of 30 bar, WHSV of 2.3 h^{-1}, and H_2/feed molar ratio of 40). Rautanen et al. [21] reported the kinetics of the tetralin hydrogenation in decane over Ni/Al$_2$O$_3$ catalyst in the temperature range of 85–160°C and a pressure range of 20–40 bar; the hydrogenation proceed by sequential steps from tetralin to *cis*- and *trans*-decalins with the formation of octalins as reaction intermediates. Besides the hydrogenation products, Gault et al. also observed the formation of some naphthalene by the dehydrogenation of tetralin. Within a series of noble metals investigated by Gault et al. [22], Ir displayed the strongest tendency to break unsubstituted C–C bonds; McVicker et al. [23] evaluated that 0.9 wt% Ir/Al$_2$O$_3$ catalyst is highly active for the production of RO products.

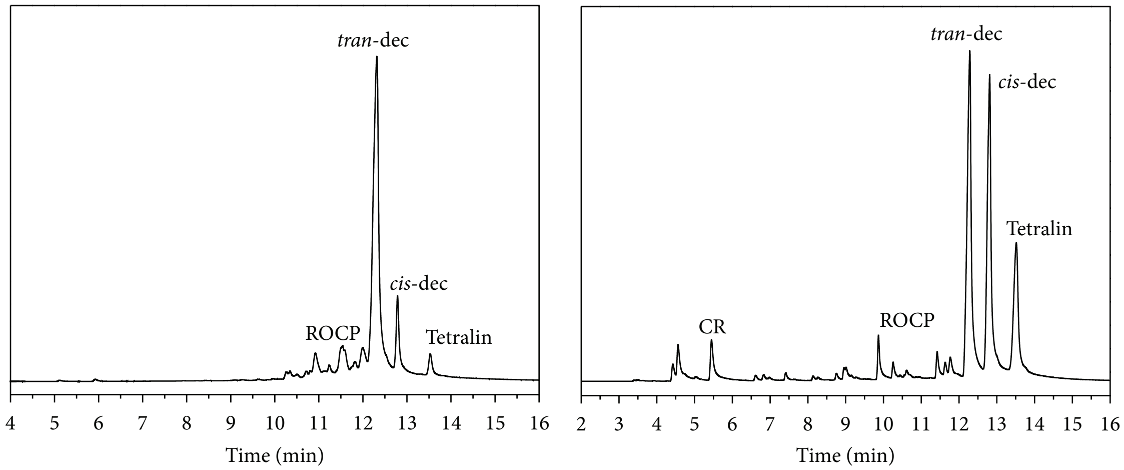
Figure 3 shows the section of the gas chromatogram of the reaction products formed during the hydroconversion tetralin over Ni/SiO$_2$ and Ir/SiO$_2$ catalysts. *trans*-decalin and *cis*-decalins are obtained as major products. The peak separation is shown in the GC chromatograms of the liquid products obtained during the hydrogenation of tetralin on both the catalysts. CR products are related to the organic compounds with fewer carbon atoms than C10 (C1–C9). The main components of ROCP products are ring contraction (RC) and ring opening (RO). RC products consist of methylindene and octahydropentalenes having one or two C5 naphthenic rings, respectively, decalin isomers, or simply isodecalins and RO were mainly associated with C10-alkylcyclohexanes and C10-alkylcyclopentanes. ROCP products are the most important products in the point of view of CNs. The results for the hydrogenation of tetralin over both Ni/SiO$_2$ and Ir/SiO$_2$ catalysts are presented in Figure 4. It is clearly seen that the conversion and total decalin selectivity were higher with Ni/SiO$_2$ as compared to Ir/SiO$_2$. In case of Ir/SiO$_2$ catalyst, we obtained 85% conversion of tetralin with 75.1% of decalin along with 13.3% of ROCP and 11.6% of



(a)

(b)

Figure 2: HR-TEM images of reduced (a) Ni/SiO_2 and (b) Ir/SiO_2 catalysts.



(a)

(b)

Figure 3: Gas chromatogram of the tetralin hydroconversion over (a) Ni/SiO_2 and (b) Ir/SiO_2 catalysts, reaction conditions: $T = 270^\circ C$, $P = 30$ bar, WHSV = $1.8\,h^{-1}$, H_2/feed molar ratio = 40, (ROCP-ring opening/ring contraction products, CR-cracking products).

CR. Whereas Ni/SiO_2 catalyst showed slightly higher 88.3% of tetralin conversion and higher 93% of decalin products selectivity with 7% of ROCP, without any CR products. In term of isomers selectivity, Ni/SiO_2 catalyst produces 74.1% *trans*-decalin and 19.1% *cis*-decalin (*trans*/*cis* ratio = 3.7), whereas Ir/SiO_2 catalyst catalyst gives 39.3% *trans*-decalin and 35.8% *cis*-decalin (*trans*/*cis* ratio = 1.1).

The *trans*-decalins are the most desired products than *cis*-decalin for jet fuel as they are stable at high temperatures. But as per above discussion in the introduction part *cis*-decalin is more desired intermediate for the improvement of diesel quality and CN; ROCP products are the most desired products from tetralin hydroconversion. *cis*-decalin shows higher reactivity towards ring opening than *trans*-decalin. The main possible reason for the enhancement of ROCP and CR selectivity over Ir/SiO_2 catalyst was considered, and it is due to the Ir displayed the strongest tendency to break unsubstituted C–C bonds than Ni. Rautanen et al. [21] also reported that CR products were not produced during hydrogenation of tetralin over Ni/Al_2O_3 catalyst.

The effect of different support for Ir, such as Ir/SiO_2, Ir/ASA, and Ir/USY zeolites, on the ROCP selectivity was also studied and the results are presented in Figure 5. It has been widely accepted that the ring opening of naphthenic on acidic catalysts proceeds via a ring contraction step in which the six-member ring is converted into a five-member ring before their opening. From Figure 4, it is clearly seen that the conversion and ROCP selectivity were higher with Ir/USY as compared to Ir/SiO_2 and Ir/ASA catalyst. The main possible reason for the enhancement of activity by Ir/USY was considered due to the presence of higher strong acidic strength, which is higher than that of the other two catalysts.

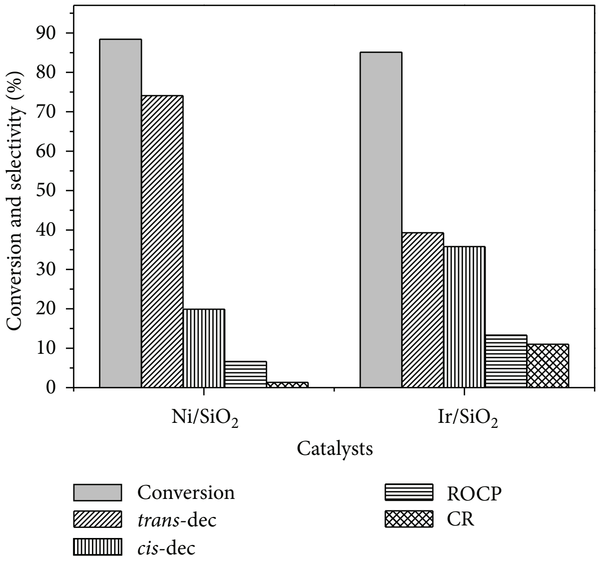


FIGURE 4: Conversion and selectivity of tetralin over Ni/SiO_2 and Ir/SiO_2 catalysts, reaction condition: $T = 270^\circ C$, $P = 30$ bar, WHSV = $1.8\,h^{-1}$, H_2/feed molar ratio = 40, (ROCP—ring opening/ring contraction, CR—cracking products).

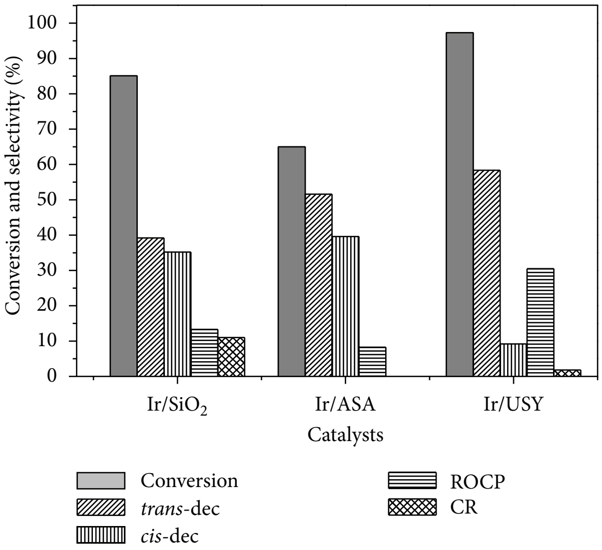


FIGURE 5: Conversion and selectivity of tetralin over Ir/SiO_2, Ir/ASA and Ir/USY catalysts, reaction condition: $T = 270^\circ C$, $P = 30$ bar, WHSV = $1.8\,h^{-1}$, H_2/feed molar ratio = 40, (ROCP—ring opening/ring contraction, CR—cracking products).

The total acidic strength (acid sites population) seems to be the main responsible factor for the increase of tetralin conversion [18]. Further detaild study on the effect of acidity and detailed characterization of support material are going on to achieve maximum yield of ROCP products.

4. Conclusion

The hydrogenation and SRO of tetralin have been investigated over Ni/SiO_2 and Ir/SiO_2 catalysts. In both catalysts, *cis*- and *trans*-decalins were obtained as major products from tetralin hydrogenation. Ni/SiO_2 shows an excellent conversion and high selectivity for the hydrogenation products of tetralin under mild reaction condition. The Ir/SiO_2 catalyst gave 85% of tetralin conversion and 75.1% of decalin products selectivity whereas Ni/SiO_2 catalyst showed an unprecedented high catalytic performance with 88.3% of tetralin conversion and 93% of decalin products selectivity. Ir/SiO_2 catalyst shows good selectivity for *cis*-decalin which is desired intermediate products for the improvement of diesel quality and CN. The higher dispersion of metallic nano particles on the supports allows their low temperature reduction and hence the higher hydrogenation activity at controllable reaction conditions.

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