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Catalysis Today 101 (2005) 65–71

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The effect of cerium, lanthanum and zirconium on nickel/alumina catalysts for the hydrogenation of carbon oxides

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Abstract

A series of nickel/alumina catalysts promoted with cerium, lanthanum and zirconium was studied in relation to CO and CO_2 hydrogenation. The following examinations were applied in the studies: temperature-programmed reduction (TP reduction), X-ray diffraction, TP desorption of pre-adsorbed hydrogen, adsorption of O_2 and its TP hydrogenation, thermal effect of O_2 adsorption, adsorption of CO and its TP desorption or TP hydrogenation, and testing of activity in CO and CO_2 hydrogenation. The examinations of O_2 and CO adsorption demonstrate that the promoters decrease rate but do not affect quantity of the adsorption. On the other side, the promoters do not affect TP desorption of hydrogen and TP hydrogenation of pre-adsorbed oxygen which indicates that the promoters do not modify the state of oxygen and hydrogen adsorbed on nickel. At the same time, the TP desorption of CO demonstrates that, contrary to zirconium, cerium and lanthanum considerably promote dissociation of CO. The effect very likely is responsible for higher activity of the catalysts in TP hydrogenation of pre-adsorbed CO and also in the steady state activity of the catalysts in CO and CO_2 hydrogenation.

Keywords: Nickel/alumina catalysts; Cerium, lanthanum and zirconium promoters; Hydrogenation of CO and CO_2

1. Introduction

Nickel/alumina catalysts are commonly used in two processes involved in hydrogen production: steam reforming of methane and purification of obtained hydrogen from traces of carbon oxides. In view of the enormous scale of these processes, any improvement of the catalysts is highly desired. Valuable suggestions concerning that problem ensue from literature data. First, it was demonstrated that cerium and lanthanum promote activity of nickel/alumina catalysts in CO hydrogenation [1–4], the reaction reverse to steam reforming of methane. Second, it was reported that cerium, lanthanum and zirconium promote various metal catalysts in dry reforming of methane [5–10], increasing their thermal stability, resistance to carbon deposition and catalytic activity [11–14]. The examinations, however, have not explained the role of the promoters in the catalysts.

This study concerns the effect of cerium, lanthanum and zirconium on chemical properties of nickel/alumina catalysts in the belief that the examinations clarify the reasons of high activity of the promoted catalysts in CO and CO_2 hydrogenation [13,14]. The measurements were carried out using model nickel/alumina catalysts prepared by impregnating 90% NiO/Al_2O_3 material [15] with aqueous solutions of Ce, La and Zr nitrates. Low alumina content in these specimens was favourable in studies of the effect of the promoters on chemical properties and catalytic activity of nickel/alumina catalyst.

2. Experimental

2.1. Apparatus

Chemical characterization of the catalysts was carried out in a glass flow system equipped with a gradientless microreactor [16,17]. A temperature controller maintained

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doi:10.1016/j.cattod.2005.01.003

the reactor temperature within 1 °C and provided linear temperature programming in the range of −200 to 800 °C; low temperature was obtained cooling the applied furnace with liquid nitrogen. Hydrogen, helium and argon were of 99.999% purity, and carbon monoxide and carbon dioxide were of 99.99% purity. Hydrogen was further purified by Trienco Hydrogen Purifier equipped with thick wall palladium alloy tubing. Argon and helium were purified in a series of columns packed with Cu/SiO_2, silica gel and molecular sieves 5 Å. The gas stream required was fed to the measuring system by a four-way valve and, before entering the reactor, it was additionally purified from traces of oxygen and water by passing through an MnO/SiO_2 column. In the case of a He stream, the column was maintained at −195 °C, which lowered the content of impurities below 0.1 ppm. The composition of the gas stream leaving the reactor was monitored by means of a TCD cell and the results were collected by a computer-controlled system.

2.2. Materials

The promoted precursors were prepared using 90% NiO/Al_2O_3 material. The material was obtained by co-precipitation method, mixing aqueous solution of Na_2CO_3 with $Ni(NO_3)_2$ and $NaAlO_2$ solution [15]. The precipitate was thoroughly washed, spray-dried and calcined in the air at 400 °C for 2.5 h. Analysis of the obtained material showed below 0.05 wt.% of Na_2O. The promoters, i.e. cerium, lanthanum and zirconium were introduced by impregnation of 90% NiO/Al_2O_3 material with aqueous solutions of $Ce(NO_3)_3$, $La(NO_3)_3$ and $Zr(NO_3)_2$. The stirred suspension was dried and then calcined in the air (400 °C, 2 h) to decompose the nitrates to respective oxides. Concentration of the promoters in the obtained precursors, expressed as elementary molar fraction, $X/(X + \mathrm{Ni} + \mathrm{Al})$, was equal to 0.04.

2.3. Measurement procedure

2.3.1. TP reduction of calcined precursors

Typically, 50 mg of the precursor was used for chemical characterization. The sample was in situ dried at 400 °C for 0.5 h and then pre-reduced in an 80% $H_2 + Ar$ stream of 1 cm^3/s. The reduction was carried out at linearly increasing temperature of 0.17 °C/s from −25 to 500 °C, whereupon it was continued at constant temperature of 500 °C for 2.5 h. The stream leaving the reactor was dried in a −78 °C trap and consumption of hydrogen was measured. Each TP measurement was terminated by determination of final position of the base line and respective response of TCD cell.

Systematic characterization of the reduced catalyst was preceded by a treatment consisting of passivation with portions of 1.65 μmol O_2 and depassivation with an 80% $H_2 + Ar$ stream, which resulted in lower, but stable, dispersion of nickel. Every subsequent examination was initiated with an extra reduction of examined sample in a H_2 stream (0.5 cm^3/s, 480 °C, 0.5 h). The reduced sample was purged from the adsorbed hydrogen in a He stream (0.5 cm^3/s, 400 °C, 0.5 h), whereupon one of the following measurements was performed.

2.3.2. TP desorption of pre-adsorbed hydrogen

Adsorption of hydrogen was carried out at atmospheric pressure in three stages: (A) initially at constant temperature of 150 °C for 0.25 h; (B) at gradually decreasing temperature (during 0.25 h) from the initial value to 25 °C; and (C) at constant temperature of 25 °C for 0.25 h. After the adsorption, the examined sample was flushed with a He stream (0.5 cm^3/s, 25 °C, 0.25 h) to remove weakly adsorbed hydrogen and strongly adsorbed hydrogen was examined by TPD method. The examination, TPD–H_{ads}, was carried out in an Ar stream of 0.5 cm^3/s at linearly increasing temperature of 0.17 °C/s from −25 to 480 °C.

2.3.3. Adsorption of dioxygen and its TP hydrogenation

The adsorption was carried out by the pulse method, introducing every 60 s portions of 1.65 μmol O_2 into a He stream (0.5 cm^3/s) flowing over the sample maintained at 0 °C. For selected samples the examinations were carried out with the aid of a special microreactor that allowed simultaneous measurement of O_2 adsorption and accompanying thermal effect [18]. In these measurements larger portions of 4.5 μmol of O_2 were introduced into a He stream, flowing over the sample maintained at 25 °C. Calibration of these measurements was performed, assuming that thermal effect of O_2 adsorption on nickel/alumina catalyst equals 100 kcal/mol [19,20].

The hydrogenation of pre-adsorbed oxygen, TPH–O_{ads}, was carried out in an 80% $H_2 + Ar$ stream of 0.5 cm^3/s at linearly increasing temperature of 0.17 °C/s from −25 to 480 °C. The stream leaving the reactor was dried in a −78 °C trap and consumption of hydrogen was measured.

2.3.4. Adsorption of carbon monoxide and its TP desorption or TP hydrogenation

The adsorption was carried out by the pulse method, introducing every 180 s portions of 4.5 μmol CO into a He stream (0.5 cm^3/s) flowing over the sample maintained at 25 °C. The stream leaving the reactor was passed through a 90 °C trap to decompose any $Ni(CO)_4$ that may appear during CO adsorption.

The desorption of pre-adsorbed CO, TPD–CO_{ads}, was carried out in an He stream of 0.5 cm^3/s at linearly increasing temperature of 0.17 °C/s, from −25 °C to 480 °C, whereupon it was continued at constant temperature of 480 °C for 0.33 h. The stream leaving the reactor contained not only CO but also CO_2. A micro-trap placed between the reactor and detector was alternatively kept at 25 °C or −195 °C, which allowed a fairly continuous measurement of both CO and CO_2 concentration.

The hydrogenation of pre-adsorbed CO, TPH–CO_{ads}, was carried out in an H_2 stream of 0.5 cm^3/s at linearly increasing temperature of 0.17 °C/s from −25 to 480 °C. The stream leaving the reactor was dried in a −78 °C trap and concentration of CH_4 and traces of CO was measured.

2.3.5. XRD examinations

After the chemical characterization, selected samples were passivated with O_2 pulses and subsequently examined by the XRD method. The studies were performed with Siemens D5000 diffractometer using Cu Kα radiation and graphite monochromator. The measurements were carried out with the aid of metal camera allowing simultaneous kinetics and XRD studies [21,22]. The examined sample was in situ depassivated in an H_2 stream (1 cm^3/s, 400 °C, 0.5 h) whereupon temperature of the sample was decreased to 150 °C, and XRD spectra were recorded by means of a position sensitive detector INEL CPS120. The mean size of Ni crystallites was calculated from Scherrer equation, using full width at half maximum for Ni(1 1 1) and Ni(2 0 0) reflections. The size of Ni crystallites was used to evaluate nickel dispersion, applying the relation proposed by Borodziński and Bonarowska [23].

2.3.6. Activity in CO and CO_2 hydrogenation

The activity was tested at atmospheric pressure, using a gradientless microreactor [17]. The sample of calcined catalyst (10 mg) was in situ reduced in a H_2 stream (1 cm^3/s, 400 °C, 4 h), whereupon the reactor temperature was decreased to a selected value and the H_2 stream was replaced with 0.5% CO + H_2 or 0.5% CO_2 + H_2 stream of 1.5 cm^3/s. The stream leaving the reactor was analysed (CO, CO_2 and CH_4) with an on line gas chromatograph equipped with a methanator and FID detector.

3. Results and discussion

3.1. TP reduction of calcined catalysts

Previous studies of high loaded nickel/alumina precursors have shown that the applied 90% NiO/Al_2O_3 material contains nickel mainly as crystalline NiO covered with $x\mathrm{NiO}\cdot\mathrm{Al_2O_3}$ species [15]. Fig. 1 shows TPR spectra of un-promoted (Ref.) and Ce-, La- and Zr-promoted catalysts. The examinations show that, contrary to zirconium, cerium and lanthanum retard the reduction. The effect is rather small, indicating a weak chemical interaction of lanthanum and cerium with nickel oxide. XRD patterns of the reduced catalysts (Fig. 2, for un-promoted and La-promoted catalysts) show prominent reflections of Ni phase and minute reflections of $x\mathrm{NiO}\cdot\mathrm{Al_2O_3}$ species. In the case of lanthanum-promoted catalyst, additional reflections appear at low 2Θ angles. Identical reflections were ascribed previously to $\mathrm{La_2O_3}\cdot2\mathrm{CO_2}\cdot x\mathrm{H_2O}$ phase [3]. Width of Ni reflections for un-promoted and La-promoted sample is identical, indicating no effect of lanthanum on nickel dispersion.

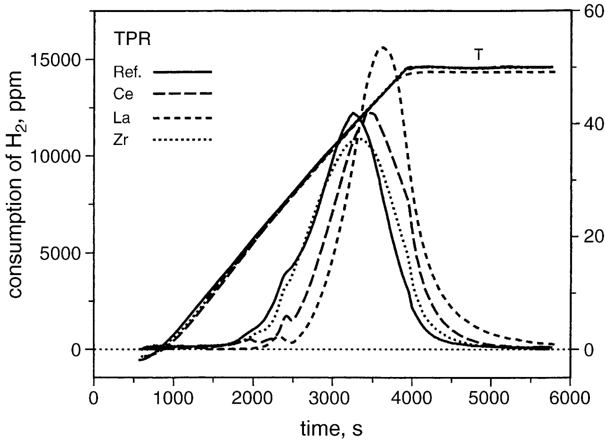

Fig. 1. TPR spectra of un-promoted and Ce, La and Zr-promoted catalysts.

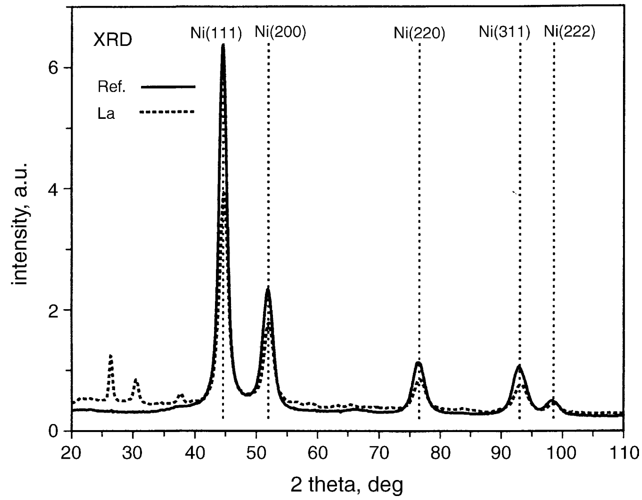

Fig. 2. XRD patterns of un-promoted and La-promoted catalysts.

The examinations in Fig. 1 do not provide any suggestions on the reduction of cerium, lanthanum and zirconium oxides. Some indications concerning that problem were obtained from TPR tests of Ce, La and Zr oxides supported on γ-alumina (the samples were prepared in the same way as the promoted catalysts; concentration of the promoter, expressed as elementary molar fraction, $X/(X + \mathrm{Al})$, was equal to 0.04). These tests showed that: (i) about 20% of supported CeO_2 was reduced to Ce_2O_3 in the range of 200–500 °C, changing colour of the sample from yellow to brown and (ii) supported lanthanum and zirconium oxides were not reduced. These results were confirmed by subsequent re-oxidation of these samples. The examinations, performed by pulse method at temperature increasing step by step, showed that: Ce_2O_3 adsorbed readily O_2, forming back CeO_2 while supported La and Zr oxides did not adsorb O_2.

3.2. Temperature-programmed desorption of hydrogen

The TPD–H_{ads} spectra obtained for the examined catalysts (Fig. 3) represent broad profiles that begin close to the flushing

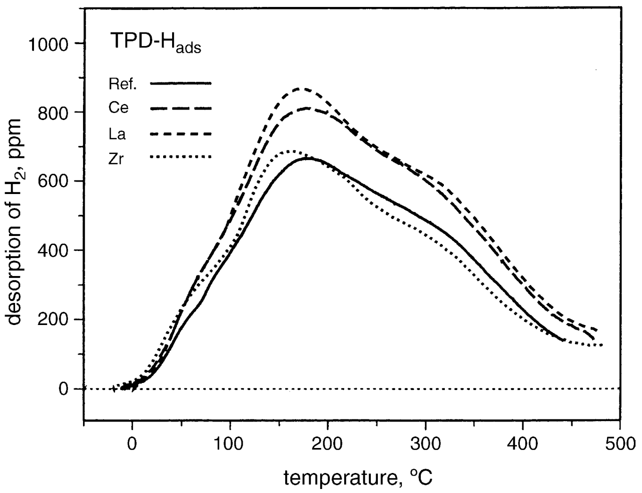

Fig. 3. TPD-H_{ads} spectra for un-promoted and Ce-, La- and Zr-promoted catalysts.

temperature, 25 °C, and decay near to the purging temperature, 400 °C. The spectra show that zirconium does not affect hydrogen adsorption whereas cerium and lanthanum slightly enhance H_2 uptake. Setting aside the question of quantity of hydrogen adsorption, the similarity of the shape of the spectra in Fig. 3 indicates that the promoters do not influence the interaction of hydrogen with nickel surface.

3.3. Adsorption and TP hydrogenation of oxygen

Adsorption of dioxygen on nickel is extremely fast, highly exothermic process. Our examinations confirmed that view for un-promoted sample as large number of O_2 pulses was adsorbed fully and subsequent O_2 pulses were adsorbed in a small part (Fig. 4A, for un-promoted catalyst). In contrast to this, identical measurement (Fig. 4B for La-promoted catalyst) showed that the applied promoters slow down O_2 adsorption but do not affect quantity of O_2 adsorption. Complementary studies showed that further grinding of the sample did not increase the adsorption rate, which indicates chemical nature of the effect.

Additional data on O_2 adsorption on La-promoted catalyst were obtained from the examination of thermal effect of the interaction (Fig. 5). Setting aside gradual decrease of the effect, which is related to imperfect manufacture of the reactor used in the measurements [18], the examinations showed that heat of O_2 adsorption on un-promoted sample and on La-promoted sample is identical. This indicates that the same chemical reaction takes place on these samples and lanthanum affects only the rate of the reaction. The decrease of the rate of O_2 adsorption on promoted samples very likely originates from different decoration of nickel surface. It is known that nickel crystallites in Ni/Al_2O_3 are decorated with $x NiO{\cdot}Al_2O_3$ species [15,16,25,26] and it is plausible that additional species such as $x_1 NiO{\cdot}La_2O_3$ or $x_2 NiO{\cdot}Al_2O_3{\cdot}La_2O_3$ appear on nickel surface of La-promoted sample. It seems that the observed effect of lanthanum on the rate of O_2 adsorption (Figs. 4 and 5) ensues from an electronic or steric effect produced by the decorants.

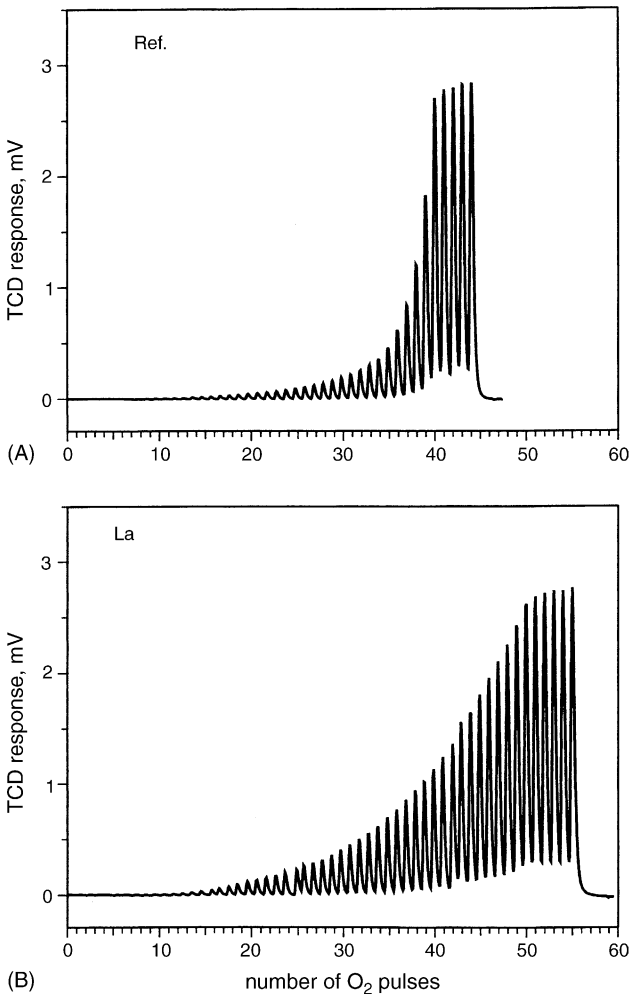

Fig. 4. Progress of O_2 adsorption: (A) un-promoted catalyst and (B) La-promoted catalyst.

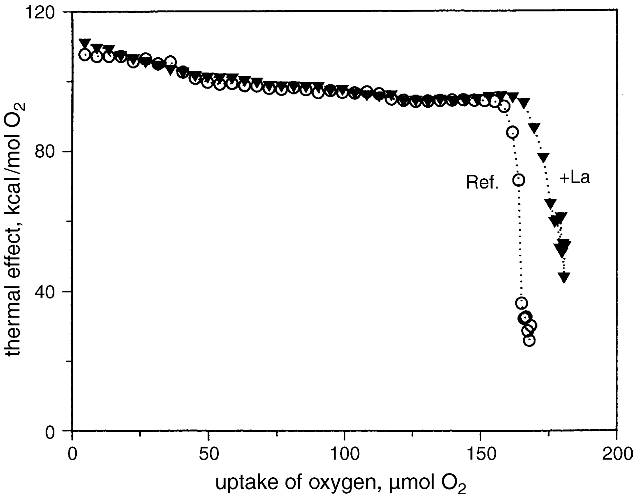

Fig. 5. Thermal effect of O_2 adsorption: (A) un-promoted catalyst and (B) La-promoted catalyst.

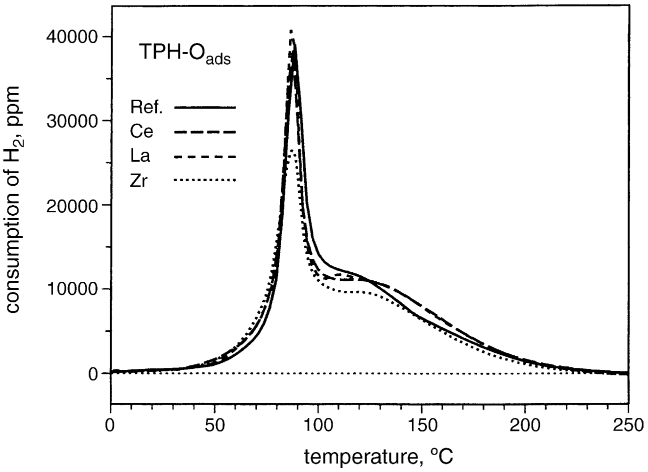

Fig. 6. TPH-O_{ads} spectra for un-promoted and Ce-, La- and Zr-promoted catalysts.

Fig. 6 shows TP hydrogenation of pre-adsorbed oxygen. According to the previous studies of Ni/Al_2O_3 catalysts [27] the sharp peak at 90 °C reflects the hydrogenation of surface nickel oxide and the profile at about 140 °C corresponds to hydrogenation of surface nickel aluminate, which forms in the course of the reaction. The spectra in Fig. 6 show that the promoters hardly affect both the hydrogenation of the surface nickel oxide and also the formation and hydrogenation of the surface nickel aluminate.

3.4. Adsorption and TP desorption or TP hydrogenation of carbon monoxide

It is commonly accepted that at room temperature carbon monoxide adsorbs on nickel in molecular form. At low temperature the adsorption may be accompanied by formation of $Ni(CO)_4$ and at high temperature by dissociation and disproportionation of CO [28]. Our examinations show that adsorption of CO is fast for un-promoted catalyst while for promoted catalysts it is initially fast and subsequently slow (Fig. 7 for un-promoted and La-promoted catalysts). Similarly as in the case of O_2 adsorption, the examinations show that the promoters slow down rate of the interaction but do not affect the quantity of CO adsorption.

The TP desorption of carbon monoxide (Fig. 8) reflects a number of processes taking place in the course of the test. Previous studies of Ni/Al_2O_3 catalysts [28] have shown that: (i) CO profile at 0–150 °C represents desorption of molecularly adsorbed CO, (ii) CO profile over 200 °C reflects association of C atoms adsorbed on nickel with O atoms adsorbed on nickel or at metal–support boundary, (iii) CO_2 profile at 150–450 °C reflects reaction of CO molecules with O atoms to CO_2, and (iv) dissociation of pre-adsorbed CO diminishes the desorption of CO and provokes oxidation of CO to CO_2.

The TPD–CO_{ads} spectra presented in Fig. 8 demonstrate that, contrary to zirconium, cerium and lanthanum considerably affect CO and CO_2 evolution. The effects indicate that cerium and lanthanum promote CO dissociation at low temperature and enhance CO and CO_2 formation at high temperature. Accepting the common view that dissociation of CO controls the rate of CO hydrogenation, the TPD–CO_{ads} tests suggest higher activity of Ce$^-$ and La-promoted catalysts in CO hydrogenation.

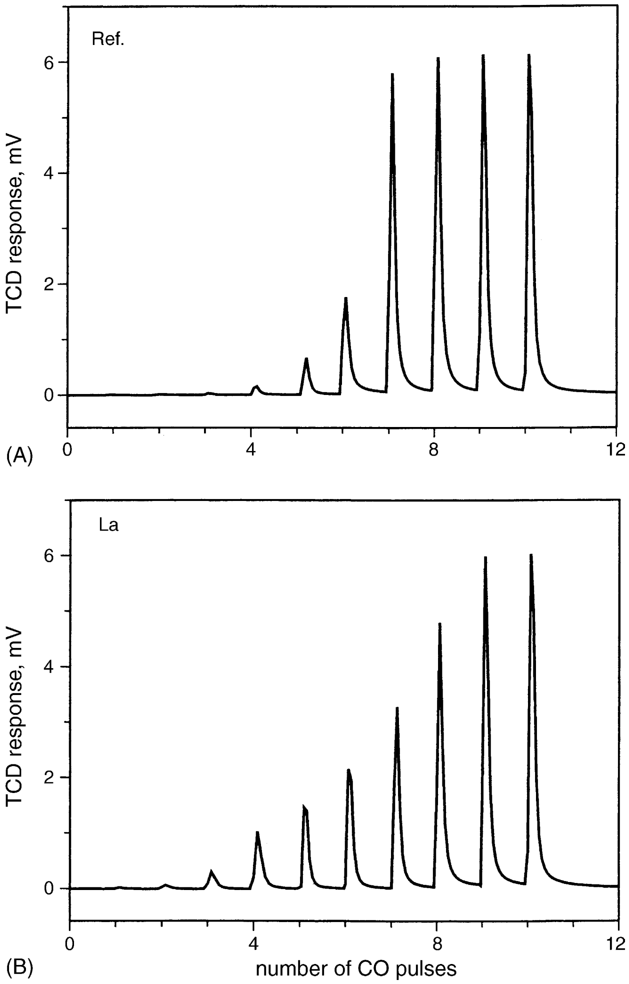

Fig. 7. Progress of CO adsorption: (A) un-promoted catalyst and (B) La-promoted catalyst.

Quantitative analysis of the spectra in Fig. 8 shows that at terminal temperature of the examinations the desorption degrees of C and O elements are about 0.7–0.8 and 1.0–1.1, respectively. The desorption degree of oxygen above unity indicates that additional reduction of xNiO·Al_2O_3 species with carbon takes place.

The TP hydrogenation of pre-adsorbed CO (Fig. 9) shows that, contrary to zirconium, cerium and lanthanum promote the hydrogenation of pre-adsorbed CO. The observed shift of the TPH–CO_{ads} profile, 10 °C for Ce and 15 °C for La-promoted samples, appear small, however, it may manifests in significant increase of the steady-state rate of CO and CO_2 hydrogenation. Integration of the spectra in Fig. 9 show that carbon was quantitatively evolved (in the form of CO and CH_4) from Ce$^-$ and La-promoted samples. In the case of Ref. and Zr-promoted samples the degree of C evolution was 0.91 and 0.95, respectively.

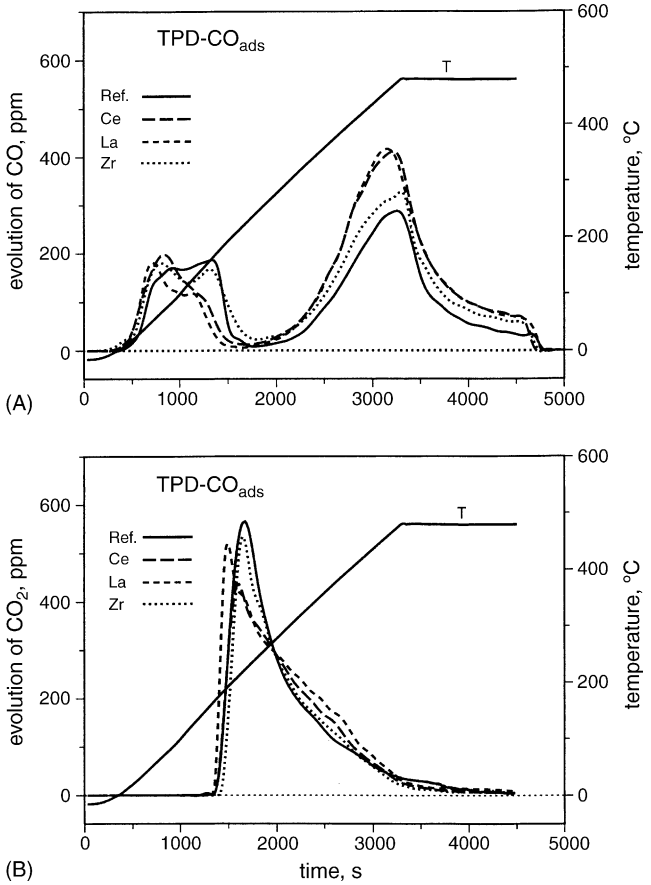

Fig. 8. TPD–CO$_{ads}$ spectra for un-promoted and Ce-, La- and Zr-promoted catalysts: (A) evolution of CO; (B) evolution of CO$_2$.

3.5. Dispersion of nickel

The measurements of oxygen, carbon monoxide and hydrogen adsorption were used to evaluate nickel dispersion (the fraction exposed), using the adsorption stoichiometries reported for un-supported nickel: $O/Ni_s = 1,7$ [24], $CO/Ni_s = 0.5$ [29] and $H/Ni_s = 1$. The obtained values, together with the results found from XRD measurements, are presented in Fig. 10. The examinations show that the promoters have a minor effect on nickel dispersion, which

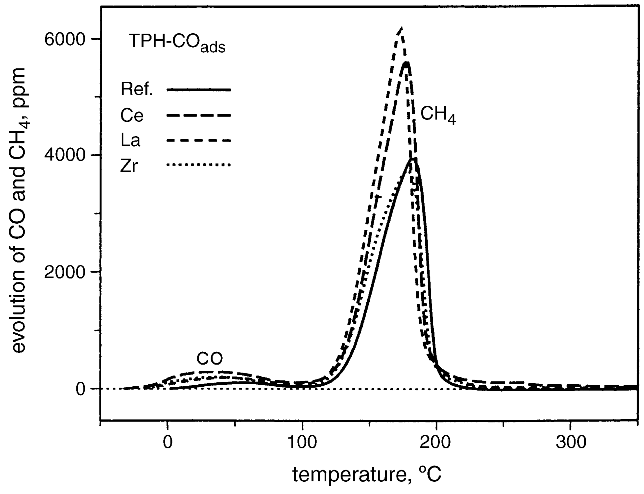

Fig. 9. TPH–CO$_{ads}$ spectra for un-promoted and Ce-, La- and Zr-promoted catalysts.

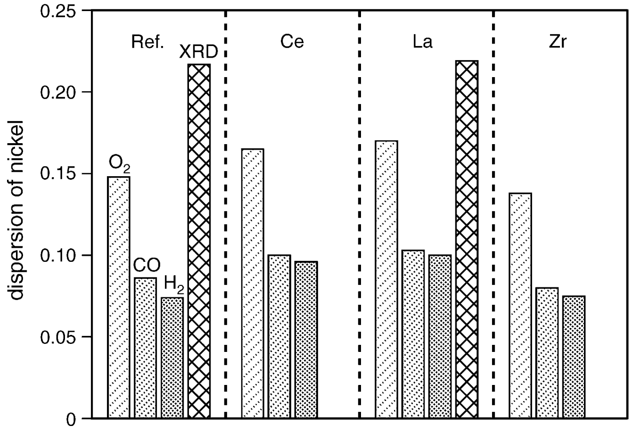

Fig. 10. Dispersion of nickel in un-promoted and Ce-, La- and Zr-promoted catalysts.

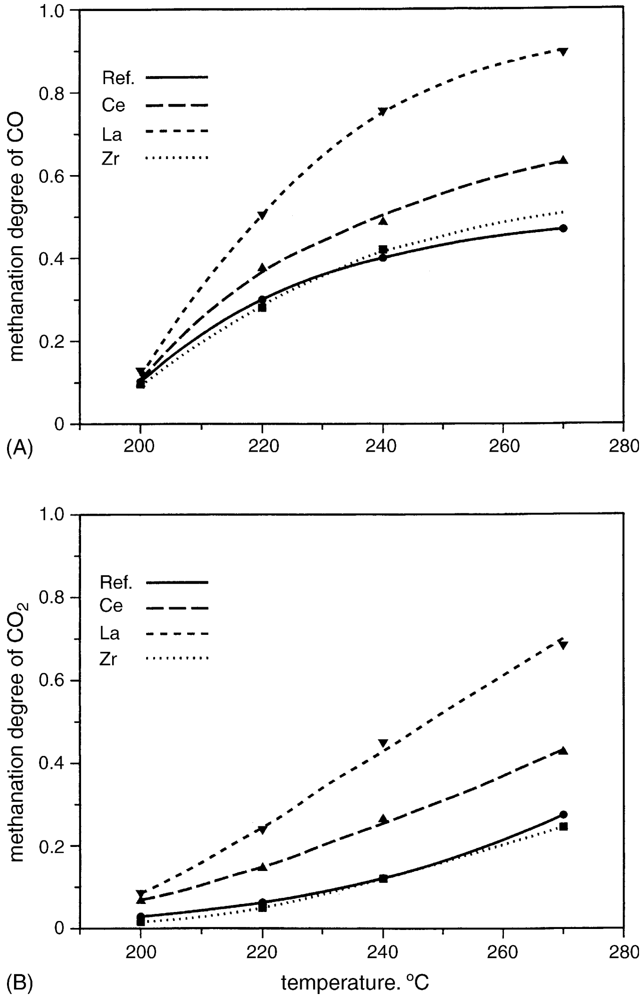

Fig. 11. Activity of un-promoted and Ce-, La- and Zr-promoted catalysts: (A) CO hydrogenation and (B) CO$_2$ hydrogenation.

means that alumina plays a crucial key role in supporting high dispersion of nickel in promoted catalysts. In addition, the comparison shows that dispersion derived from the adsorption measurements is considerably lower than that found from the XRD measurements and this suggests that decoration of Ni crystallites with alumina species diminishes adsorption ability of nickel. A comparison of the measurements in Fig. 10 with analogous measurements performed for Ni powder indicates that alumina decorants reduce adsorption ability of nickel, and the scale of the effect increases in the order: O_2, CO, H_2.

3.6. Hydrogenation of CO and CO_2

The main product of the steady state hydrogenation of CO and of CO_2 was methane. Apart from methane, traces of CO_2 were produced in the course of CO hydrogenation, and traces of CO in the course of CO_2 hydrogenation. The measurements presented in Fig. 11 show that, in contrary to zirconium, cerium and lanthanum considerably increase conversion of CO and CO_2 to methane. These results are in line with the suggestions derived from TPD–CO_{ads} test and also TPH–CO_{ads} test (Figs. 8 and 9). The key role of CO dissociation in the hydrogenation of CO and also in the hydrogenation of CO_2 needs detailed examinations of kinetics of the reactions.

4. Conclusions

The presented studies characterize the effect of cerium, lanthanum and zirconium on nickel/alumina catalysts with respect to CO and CO_2 hydrogenation. The examinations of O_2 and CO adsorption demonstrate that the promoters decrease rate but do not affect quantity of the adsorption (Figs. 4, 5 and 7). On the other side, the promoters do not affect TP desorption of hydrogen and TP hydrogenation of pre-adsorbed oxygen (Figs. 3 and 6) which indicates that the promoters do not modify the state of hydrogen and oxygen adsorbed on nickel. At the same time, the TP desorption of pre-adsorbed CO (Fig. 8) demonstrates that, contrary to zirconium, cerium and lanthanum considerably promote dissociation of CO. The effect manifests itself in enhanced activity of the catalysts in TP hydrogenation of pre-adsorbed CO (Fig. 9) and also in the steady state activity of the catalysts in CO and CO_2 hydrogenation (Fig. 11). It is worth to emphasize on rather small effect of lanthanum and cerium on the dissociation of CO in comparison to the effect of the promoters on the steady-state activity in CO and CO_2 hydrogenation. This disproportion shows that particular care is necessary in chemical characterization of catalysts when explanation of catalytic activity is the aim of the studies.

Acknowledgement

The Polish State Committee for Scientific Research (KBN) has supported this work financially under research grant number PBZ/KBN/018//T09/99/5b.

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