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Selective isoprene hydrogenation over LnNi (Ln=Pr, Gd, Tm) intermetallic compounds

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Abstract

Isoprene hydrogenation on LnNi (Ln=Pr, Gd, Tm) rare earth intermetallic compounds has been studied. The effect of rare earth elements on nickel catalytic behaviour was investigated. The results at steady state indicate that the compounds are all more active than pure nickel. The main reaction products are 2M2B (2-methyl-2-butene) and 2M1B (2-methyl-1-butene) with a selectivity greater than 90%. The activity at t_o (initial time reaction) and the selectivity at isoprene isoactivity clearly indicate the promotion of nickel's catalytic behaviour by the rare earth element.

Keywords: Intermetallic compounds; Nickel; Lanthanides; Isoprene; Selective hydrogenation

1. Introduction

Binary intermetallic compounds of rare earth elements (or actinides) and transition metals (usually Ni, Co, Mn, or Fe) have been found to be catalytically active in a variety of reactions [1–3]. This was first demonstrated by the hydrogenation of nitrobenzene and cyclohexene carried out at the Philips Lab. using $LaNi_5$ as the catalyst [1,2]. Other important examples include the NH_3 synthesis using AB_2, AB_3, AB_5, A_2B_7, and A_2B_{17} rare earth intermetallic compounds [4], and methanation with $LaNi_5$, ANi_5 (A=Th, U, Zr), and various AB_2 catalysts [5,6].

It was also observed that binary rare earth intermetallic compounds, Ln_xM_y, decompose into rare earth oxides or nitrides leaving at their surface the transition metal M to which the catalytic activity was attributed [7,8]. This new type of supported catalysts has been also studied by our group [9,10].

In this work we studied the catalytic properties of LnNi (Ln=Pr, Gd, Tm) binary intermetallic compounds as preliminary work to understand the rare earth effect on the catalytic activity of the transition metal. Isoprene hydrogenation was chosen as a model reaction because it is a oxygen-free compound and at the same time one of the products of the hydrogenation reaction, 2-methyl-2-butene, is the main feedstock to the *tert*-amyl methyl ether (TAME) process [11,12].

2. Experimental

Isoprene was obtained from Aldrich (purity >99%) and purified by fractional distillation after refluxing over sodium. Hydrogen was obtained from Air Liquid (purity N57, >99.99%) and used as supplied. Nickel was obtained from Aldrich (powder, purity >99,99%) and used as supplied. Rare earth's were obtained from Research Chemicals (purity >99,9%) and used as supplied.

The rare earth intermetallic compounds, LnNi (Ln=Pr, Gd, Tm), were prepared by direct melting of stoichiometric amounts of the elements in an induction furnace with a levitation crucible under dynamic high vacuum (10^{-5} Torr). The melting process was repeated several times in order to ensure a perfect homogeneity. No further thermal treatment needed, e.g. annealing, since all compounds melt congruently. All the manipulations of the intermetallic compounds were carried out under N_2 inert atmosphere inside of a glove box (moisture and O_2<5 ppm).

The catalytic activity for the selective isoprene hydrogenation was measured in a fixed bed U-shaped glass reactor, with a glass frit and an inside volume of 15 cm^3, operating continuously at atmospheric pressure under gaseous flow of 2% isoprene in helium. The standard

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reagents partial pressures were $p_{H_2}=228$ Torr, and $p_{\text{isoprene}}=15.2$ Torr. Mass flow controllers were used to control H_2 and He gases flow. A thermocouple was placed near the catalytic bed for continuous monitoring of the sample temperature. Before each reaction, the intermetallic catalysts were treated in situ with pure hydrogen (2 l h^{-1}) at 250°C in order to obtain an oxygen-free metal surface.

The reaction was studied with a weight hourly space velocity (WHSV) of 1 h^{-1} (g of feed/g of catalyst h), at 250°C, with typically $m=200$ mg and particle size <200 mesh. The outlet gas composition was analysed on-line by gas chromatography with a Carbopack C/0.1% SP-1000 packed column ($L=2.0$ m, $\emptyset=1/8$ in., 80–100 mesh) using a Shimadzu 9A instrument equipped with flame ionisation detector (FID). The gaseous effluent was monitored every 60 min by means of an automated six-way sampling valve.

The reaction rate is represented as a turnover frequency (TON) in units of moles of isoprene converted per mole of catalyst per hour. The selectivity to isopentenes (S) is defined as the ratio of the moles of isopentenes (2-methyl-1-butene, 3-methyl-1-butene, and 2-methyl-2-butene) produced per mole of isoprene converted.

3. Results and discussion

The results obtained for the selective isoprene hydrogenation over LnNi (Ln=Pr, Gd, Tm) at the steady state showed that they are all more active than pure nickel (Table 1). The activity expressed as moles of isoprene converted per mole of catalyst per hour is as follows: Ni (24 h^{-1}), PrNi (83 h^{-1}), GdNi (1296 h^{-1}), TmNi (404 h^{-1}). GdNi is 3 times more active than TmNi, 16 times more active than PrNi, and 54 times more active than Ni. However, when compared with the activity over a commercial catalyst, 5%Pt/Al_2O_3, these values are very small. The platinum catalyst catalytic activity (30 000 h^{-1}, per mole of Pt), at a lower temperature (100°C) and for a WHSV 20 times superior, is 23 times higher than the activity of GdNi.

As shown in Fig. 1a,b the isoprene conversion decreases with the time-on-stream when Ni or PrNi are used, but increases for GdNi and TmNi (Fig. 1c,d). This increase of activity is currently under study but we have previously observed this effect for AB_2 type copper–rare earth intermetallic compounds [9,10]. This effect was correlated with a segregation phenomena due to the migration of copper to the catalyst surface, modification of the surface composition and enhancement of the catalytic activity (EDAX results). Ni and PrNi catalytic activity has a significant drop with time on stream, but like for GdNi and TmNi an increase in the hydrogenation selectivity to isopentenes is observed.

The main reaction products are 2-methyl-1-butene (2M1B), 3-methyl-1-butene (3M1B), 2-methyl-2-butene (2M2B) and 2-methyl-butane (isopentane) (ISO). Using the Pt commercial catalyst (5%Pt/Al_2O_3), the hydrogenation of isoprene yields the three isopentene isomers, approximately in the 1:1:2 ratio (2M1B, 23.8%; 3M1B, 21.3%; 2M2B, 46.5%), and a very small amount of isopentane (ISO, 8.4%). A simple mechanistic scheme has been suggested to explain this ratio [13]. Over the AB type nickel–rare earth intermetallic compounds the only products, at the steady state, are the isopentenes. 2M2B is the main reaction product (>64%). Moreover, 2M2B+2M1B selectivity, valuable products for the feed to the TAME process, is always greater than 90%.

In order to understand the influence of the rare earth element on the catalytic activity of these nickel catalysts we have measured the activity and selectivity after a very short period of time following the introduction of isoprene on stream. Since all catalysts achieved the steady state conditions after a very long period of time on stream (Ni, 144 h; PrNi, 96 h; GdNi, 48 h; and TmNi, 48 h) we decided to compare the results after an initial time of 30 min on stream (t_0). For this short time, we assume that we are still in the presence of the 'clean' original intermetallic surface [10,14–17].

At t_0 we observed a change on the catalytic behaviour for these three elements: PrNi (697 h^{-1}), GdNi (376 h^{-1}), TmNi (24 h^{-1}). PrNi is about 2 times more active than GdNi, and 29 times more active than TmNi (Table 1). Just as for the steady state, the isopentenes selectivity at t_0 over

Table 1
Activity and product distribution at 250°C, $p_{\text{isoprene}}=15.2$ mmHg, $p_{H_2}=304$ mmHg, and WHSV=0.75 h^{-1}, over nickel and LnNi intermetallic compounds[a]

Cat.	TON×1000[b]	ISO	3M1B	2M1B	2M2B	S (%)[c]
Ni	24 (679)	0 (71)	3 (0)	21 (7)	76 (22)	100 (29)
PrNi	83 (697)	0 (0)	4 (14)	23 (35)	75 (51)	100 (100)
GdNi	1296 (376)	0 (4)	9 (12)	26 (34)	64 (51)	99 (96)
TmNi	404 (24)	0 (0)	6 (0)	23 (21)	71 (79)	100 (100)
5%Pt/Al_2O_3[d]	8 (30 000)	8 (82)	21 (0)	24 (3)	47 (14)	92 (18)

[a] Initial (between parenthesis, $t_0=30$ min) and steady state data. ISO, isopentane; 3M1B, 3-methyl-1-butene; 2M1B, 2-methyl-1butene; 2M2B, 2-methyl-2-butene.

[b] TON, mol (isoprene) mol^{-1} (catalyst) h^{-1}.

[c] S, selectivity to isopentenes (sum of 3M1B+2M1B+2M2B).

[d] TON in mol (isoprene) mol^{-1} (Pt) h^{-1}, $T=100$°C and WHSV=20 h^{-1}.

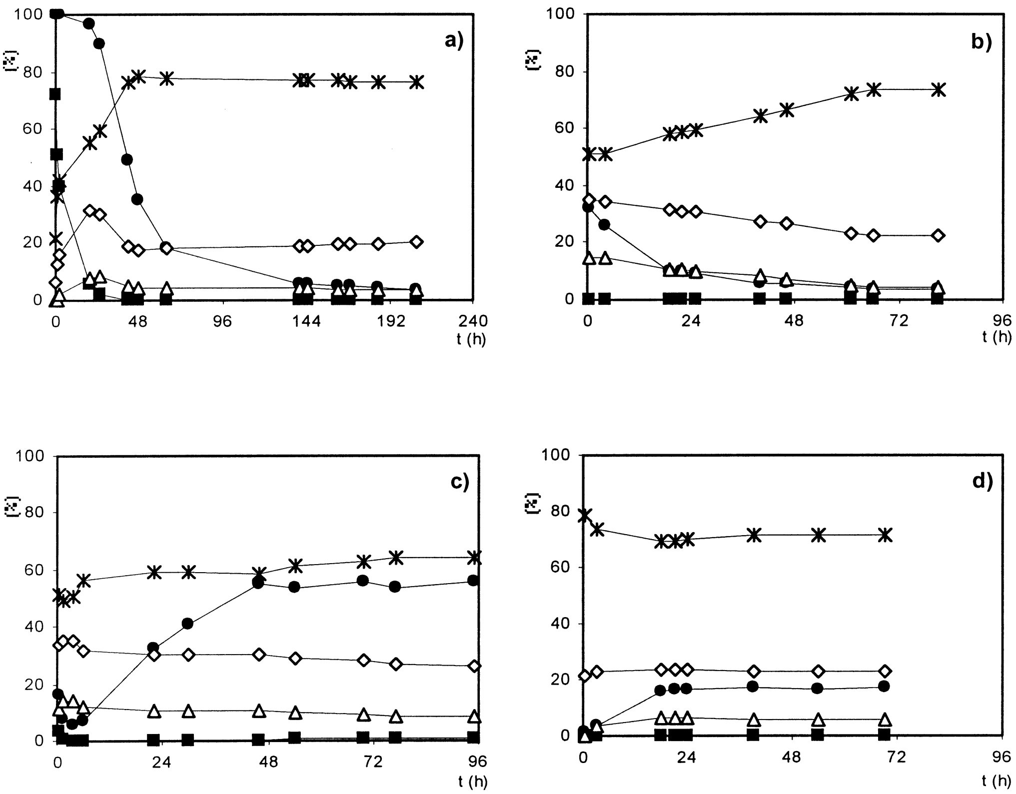

Fig. 1. Plot of isoprene conversion and selectivity to isopentenes versus time on stream for (a) Ni, (b) PrNi, (c) GdNi, and (d) TmNi. $T=250°C$, $P_{\text{isoprene}}=15.2$ mmHg; $P_{H_2}=304$ mmHg; WHSV=0.75 h^{-1}. (●) IC, isoprene conversion; (■) ISO, isopentane; (△) 3M1B 3-methyl-1-butene; (◇) 2M1B, 2-methyl-1-butene; (✱) 2M2B, 2-methyl-2-butene.

the intermetallic compounds remains very high (>96%). However, over nickel at t_0 the selectivity decreases to a rather low value (29%) with isopentane the main reaction product.

Moreover, when we compare the product distribution at isoprene isoactivity (isoprene conversion <10%) (Table 2) it is also observed that the isopentenes selectivity along the lanthanide series decreases for these three elements: PrNi (100%), GdNi (95%) and TmNi (89%).

Therefore, the above results clearly indicate that the rare earth element has an influence on the nickel catalytic behaviour for the isoprene hydrogenation.

Table 2

Isoactivity and product distribution at 250°C, $p_{\text{isoprene}}=15.2$ mmHg, $p_{H_2}=304$ mmHg, and WHSV=0.75 h^{-1}, over nickel and LnNi intermetallic compounds[a]

Cat.	TON×1000[b]	ISO	3M1B	2M1B	2M2B	*S* (%)[c]
Ni	24	0	3	21	76	100
PrNi	83	0	4	23	73	100
GdNi	72	5	5	22	68	95
TmNi	80	11	4	18	68	89

[a] ISO, isopentane; 3M1B, 3-methyl-1-butene; 2M1B, 2-methyl-1butene; 2M2B, 2-methyl-2-butene.

[b] TON, mol (isoprene) mol^{-1} (catalyst) h^{-1}.

[c] *S*, selectivity to isopentenes (sum of 3M1B+2M1B+2M2B).

4. Conclusion

Isoprene hydrogenation over LnNi (Ln=Pr, Gd, Tm) rare earth intermetallic compounds was studied. At the steady state operation conditions, they are all more active than pure nickel. The main reaction products are 2-methyl-2-butene and 2-methyl-1-butene with selectivity always greater than 90%. The results obtained at isoprene initial time on stream and isoprene isoactivity clearly indicate that the rare earth element plays a role in the nickel catalytic activity and selectivity since both decrease along the lanthanide series for the three rare earth elements studied. This work will be extended to other LnNi intermetallic compounds in order to cover the whole lanthanide series.

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