Dehydrogenation of cyclohexane over Ni based catalysts supported on activated carbon using spray-pulsed reactor and enhancement in activity by addition of a small amount of Pt

Rajesh B. Biniwale[a,b], Nobuko Kariya[b], and Masaru Ichikawa[b,*]

[a]*National Environmental Engineering Research Institute, Nehru Marg, Nagpur, 440 020, India*
[b]*Catalysis Research Center, Hokkaido University, Sapporo, 001-0021, Japan*

Dehydrogenation of cyclohexane to benzene has been carried out over Ni supported on activated carbon cloth ACC (Ni/ACC) catalysts under spray-pulsed mode reactor to study hydrogen evolution for hydrogen storage and supply system applications. The maximum rate of hydrogen evolution using monometallic Ni/ACC catalysts was 8.5 mmol g^{-1}_{cat} min^{-1} for Ni loading of 20% by weight. A small amount of Pt (0.5 wt%) was added to the Ni based catalysts. A synergistic effect was observed in the case of the promoted catalysts the hydrogen production was enhanced by ca. 1.5 times as compared to the 20 wt% Ni only catalyst. As compared to 0.5 wt% monometallic Pt catalyst, the 20 wt% Ni–0.5 wt% Pt bimetallic catalyst exhibits ca. 60 times higher hydrogen production rates. Selectivity towards dehydrogenation observed to be enhanced by addition of Pt into Ni/ACC catalysts.

KEY WORDS: cyclohexane dehydrogenation ; Ni, Pt catalysts.

1. Introduction

Storage and supply of hydrogen for fuel cells without CO is an important aspect for effective performance of PEM fuel cell systems especially when hydrogen is generated from liquid hydrocarbons by reforming reactions. The dehydrogenation of cycloalkanes such as cyclohexane, decalin and methylecyclohexane provides a good possibility for effective hydrogen storage and supply [1–6]. The advantages of the cycloalkanes include the supply of hydrogen without CO or CO_2, the aromatic products are recyclable in subsequent hydrogenation and the cycloalkanes have relatively high hydrogen contents (6–8 wt%) and are more convenient for storage and transportation due to high boiling points (80–190 °C). Due to these reasons several studies have attempted dehydrogenation of cycloalkanes for hydrogen storage and supply. Particularly, the method of hydrogen storage and supply using cycloalkanes is useful to transport the hydrogen from centralized hydrogen generation facilities to fuelling stations. Dehydrogenation of cyclohexane over Pt based catalysts has been reported earlier for storage and supply of hydrogen for fuel cells. The reaction is highly selective on Pt/activated carbon cloth and Pt/alumite catalysts with nearly 100% selectivity towards the hydrogen and benzene formation. However, from an economic point of view we have specific interests to use other metals based catalysts and to reduce the use of Pt in the catalysts. Nickel has been

reported effective for hydrocabon reforming including dehydrogenation reaction [7]. When cyclohexane is introduced over unsupported Ni, Ni–Sn and Ni/SiO_2 without H_2 flow, initially cyclohexane undergoes dehydrogenation but rapidly the selectivity to hydrogenolysis is 100% [8]. In the present study we report the high selectivity towards dehydrogenation of cyclohexane over Ni based catalysts supported on activated carbon cloth (ACC) without feeding hydrogen for maintaining reduced state of metal catalysts. Also the effect of addition of a small amount of Pt to Ni based catalysts is demonstrated.

The dehydrogenation of cycloalkanes is endothermic reaction and chemical equilibrium is favourable for dehydrogenation at higher temperature. Therefore the reactions are performed at high temperature using steady state operation under gas phase or under liquid-film state [2,3]. We have reported earlier in the case of dehydrogenation of cyclohexane [4,5] and autothermal reforming of iso-octane [9] that by feeding atomized liquid reactant in pulses, creating alternating wet and dry conditions on the heated solid catalyst surface, the yield is greatly increased. The alternate wet and dry conditions created on catalyst surface helps easy evaporation of liquid reactant on the catalyst surface. The evaporation of the reactant on catalyst surface (heaed at 250–325 °C) enriches the catalyst surface with vapor-phase reactants (b.p. 81 °C) and improves catalyst–reactant contact. Rapid volume expansion of cyclohexane due to phase change on the catalyst surface causes products and unreacted cyclohexane to be

---

* To whom correspondence should be addressed.
  E-mail: michi@cat.hokudai.ac.jp

purged from the catalyst surface. During the course of the dry step the easy removal of unreacted cyclohexane leaves a clean catalyst surface. Thus by using pulse-spray injection conditions to create alternating wet–dry conditions on the catalyst surface, an unsteady-state is created which results in high frequency factor (found in the Arrhenius expression) and show several fold increase in the reaction rate [4,5]. The unsteady state spray-pulsed mode has been used in this study by manipulating pulse injection frequency and pulse width. The catalysts were characterized using XRD, TEM and H_2 chemisorption.

2. Experimental

2.1. Catalyst preparation

Monometallic Ni catalyst used in the present study were 10 wt%, 20 wt% and 40 wt% Ni supported on an ACC with a specific surface area of 1500 m^2 g^{-1}, pore volume 0.61 cc g^{-1} and average pore size ranging between 0.6 and 1.2 nm. The Ni metal loading was achieved by incipient wetness of carbon cloth using a solution of $Ni(NO_2)_3 \cdot 6H_2O$ in acetone. The Ni impregnated carbon cloth is then dried in air. Further the catalyst was activated in H_2 flow (99.998%, 50 mL min^{-1}) following a fixed temperature cycle to reach 150 °C in 2 h, further to reach 375 °C in another 2 h and then keeping temperature at 375 °C for 4 h. In the case of bimetallic Ni–Pt catalysts the $Ni(NO_2)_3 \cdot 6H_2O$ impregnated support was heated in a N_2 flow at 300 °C, followed by impregnation with $H_2PtCl_6 \cdot 6H_2O$ solution in acetone and activated in H_2 flow following the same temperature cycle.

2.2. Reaction

The dehydrogenation of cyclohexane (reaction 1) over Ni and Ni–Pt catalysts supported on ACC (about 0.2 g of catalysts) has been carried out using pulse-spray injection conditions in this study.

The experimental setup used for cyclohexane dehydrogenation to benzene and hydrogen using spray pulse mode is shown in figure 1. The main reactor was made of glass equipped with a fine nozzle at the top for atomized injection of liquid reactant (cyclohexane). A pressure of 40 kPa was maintained in the fuel supply line to generate atomized spray. Injection frequency was controlled using a frequency generator and pulse injection width was controlled using a variable resistance arrangement. The pulse injection frequency was varied from 0.1 to 1 Hz which resulted in cyclohexane feed rate from 0.768 to 7.68 mmol min^{-1}. A carrier gas N_2 was

introduced from the top of the reactor. The catalyst was heated using a disk type heater and the catalyst temperature was held at 250–325 °C using a temperature controller and thermocouple arrangement. The unreacted cyclohexane and condensable products were collected in a reservoir connected to condenser. The product analysis was carried out using FID-GC (Shimadzu GC-14B, J&W-DB-WAX, 30 m, column i.d. 0.25 mm, film thickness 0.25 μm) and the gaseous products were periodically analyzed using a TCD micro GC (Agilent, molecular sieve 5A, 10 m).

3. Results and discussions

The results of dehydrogenation of cyclohexane at feed rate of 3.8 mmol min^{-1} (0.128 mmol pulse, 2 s intervals) over Ni monometallic, Pt monometallic and Ni–Pt bimetallic catalysts supported on activated carbon cloth are shown in table 1. Cyclohexane was efficiently dehydrogenated over Ni and Ni–Pt catalysts even without feeding hydrogen as reactant unlike the previously reported studies. A small amount of methane was also observed in the product gas, suggesting occurrence of hydrogenolysis. No other $< C_6$ hydrocarbon was observed. The selectivity towards dehydrogenation was 98.8–99.2% and 1.2–0.8% towards hydrogenolysis on various Ni monometallic catalysts. A considerable enhancement has been achieved in hydrogen production rates during dehydrogenation of cyclohexane by promoting a 20 wt% Ni catalyst with 0.5 wt% Pt (figure 2). A synergistic effect was observed for Ni–Pt bimetallic catalysts. In the case of the promoted catalyst the hydrogen production was enhanced from 8.5 mmol g^{-1}_{cat} min^{-1} to 13.1 mmol g^{-1}_{cat} min^{-1}, an increase of ca. 1.5 times. As compared to 0.5 wt% Pt monometallic catalyst the 20 wt% Ni plus 0.5 wt% Pt bimetallic catalyst exhibits ca. 60 times higher hydrogen production rates. The hydrogen selectivity was improved to 99.7% by use of the bimetallic Ni–Pt catalysts. Also the catalyst stability was improved with addition of Pt. The reaction under consideration is reversible at 300 °C and the true forward rate was estimated as;

$$r_{net} = r_f(1 - \eta)$$

where r_f is true forward rate, r_{net} is experimentally observed rate in mmol min^{-1} and

$$\eta = ([C_6H_6][H_2]^3/[C_6H_{12}])^*(1/K_{eq}).$$

The estimated forward rates over different catalysts are shown in table 1. For Ni–Pt bimetallic catalyst the

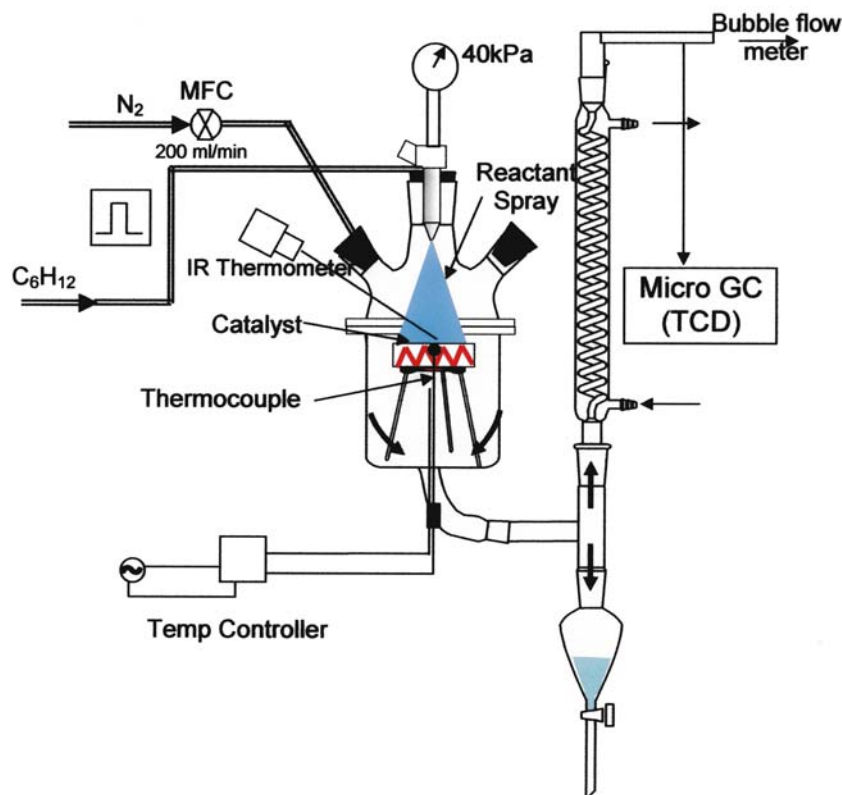Cyclohexane ⇌ Benzene + 3H_2 $\Delta H^o = +205.9$ kJ mol^{-1}
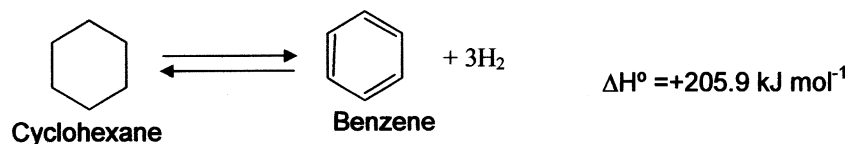
Figure 1. Experimental setup for dehydrogenation of cyclohexane under spray-pulsed condition.

Table 1

Results of dehydrogenation of cyclohexane over activated carbon supported Ni, Pt and Ni–Pt catalysts[a]

Metal loading (wt%)	H_2 Production (mmol g^{-1}_{cat} min^{-1})	Conversion of cyclohexane (%)	H_2 selectivity[b] (%)	CH_4 selectivity[b] (%)	Forward rate of H_2 production (mmol min^{-1})
10% Ni	7.1	14.4	99.1	0.9	0.51
20% Ni	8.5	21.9	98.8	1.2	0.86
40% Ni	6.8	17.5	99.2	0.8	0.59
0.5% Pt	0.22	0.4	100	0.0	0.011
20% Ni + 0.5% Pt	13.1	31.1	99.7	0.3	1.30

[a]Reaction conditions: catalyst heating temperature 300 °C, cyclohexane feed rate 3.8 mmol min^{-1} with 0.128 mmol pulse 2 s intervals.
[b]Initial selectivity at 10 min after the start of the reaction.

forward rate is 1.30 mmol min^{-1} and is highest when compared to all other monometallic catalysts used in this study.

The XRD analysis was carried out for catalysts used in the reaction and exposed to air. All the peaks of the XRD patterns of Ni monometallic catalysts (figure 3) can be assigned to Ni fcc structure (JCPDS 04-0 850) and no impurity phases such as NiO or precursor compound has been detected. Thus it is confirmed that a stable Ni catalysts has been formed. Because of the stable metallic Ni, the dehydrogenation reaction prevailed and the hydrogen produced was sufficient to maintain the activity of Ni. In the case of monometallic Ni catalysts the hydrogen production rate increased with increase in metal loading from 10 wt% to

20 wt%. However, volumetric H_2 production rates decreased at metal loading of 40 wt%. Dispersion of metal catalyst on ACC has been estimated using H_2 chemisorption and is depicted in table 2. In the case of monometallic Ni catalyst the dispersion was 1.09% for 10 wt% loading of Ni and was reduced to 0.49% and 0.43% at Ni loading of 20 and 40 wt%, respectively. The turn over frequency estimated over the surface atoms was 3.54 s^{-1} for 20 wt% Ni catalyst and was maximum for monometallic Ni catalyst. Dispersion for bimetallic Ni–Pt catalyst was 0.69% and for monometallic 0.5 wt% Pt catalyst it was 12.99%. The TOF was higher in the case of bimetallic 20 wt% Ni–0.5 wt% Pt catalyst (4.10 s^{-1}). The particle size for 40 wt% is larger (table 2) the potential cause for a
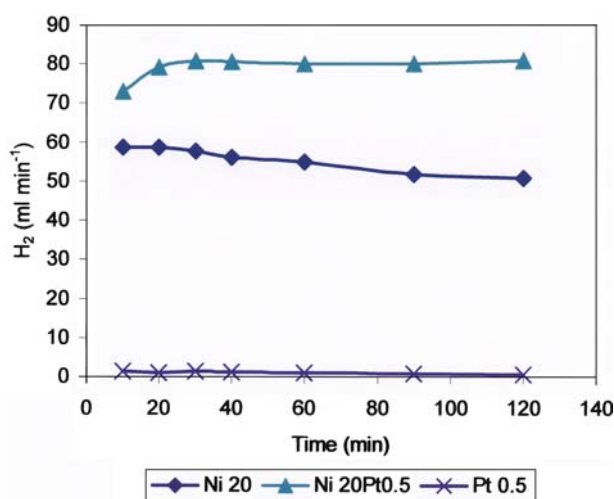
Figure 2. Hydrogen evolution rates over different catalysts under spray-pulsed reaction condition, catalysts temperature 300 °C, cyclohexane feed rate 3.8 mmol min^{-1}.
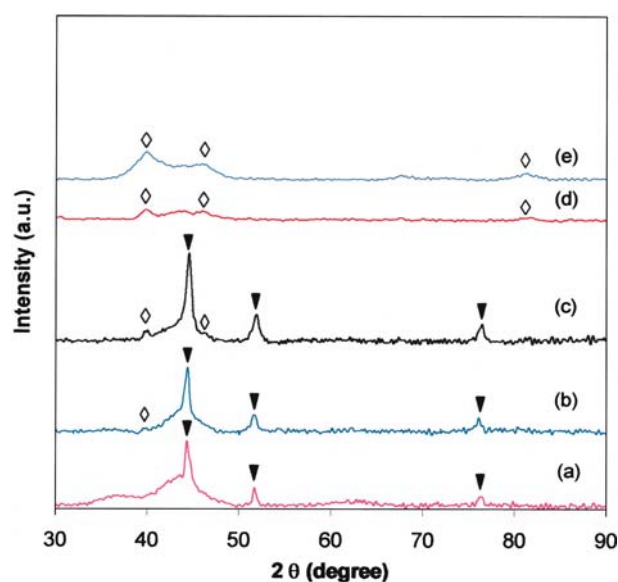

Figure 3. XRD patterns of the various catalysts on activated carbon (a) 20 wt% Ni, (b) 20 wt% Ni + 0.5 wt% Pt, (c) 20 wt% Ni + 5 wt% Pt, (d) 0.5 wt% Pt, (e) 5 wt% Pt, (peak assignment ▼ Ni, ◇ Pt).

reduction in the hydrogen production rates. The average particle size for 10 wt% and 20 wt% Ni catalyst as estimated by XRD was 10–11 nm. The particle size was about 17 nm for 40 wt% Ni catalysts. The TEM image (as shown in figure 4) for 20 wt% Ni catalyst reveals that the average particle size is ca. 10 nm, however there exists a few large particles or agglomerates of Ni with sizes of several hundred nanometers. Dehydrogenation is prevailing on dispersed Ni metal catalysts and the large particles might have contributed to the hydrogenolysis. Methane production rate decreased more rapidly as compared to hydrogen production rate as shown in figure 5. This may be explained by considering that during the reaction particle size is increased by agglomeration. Since the larger particles are responsible for structure sensitive hydrogenolysis reaction the rate of methane formation decreased considerably during the reaction period.

The mechanism of dehydrogenation of cyclohexane involves the adsorption of cyclohexane, with either simultaneous or rapid subsequent dissociation of hydrogen atoms. Adsorbed hydrogen atoms form molecules and desorbs from the surface [10]. Benzene if not desorbed quickly then undergoes further dissociation to produce methane. In the present study we have used spray-pulsed injection of cyclohexane. Before the cyclohexane is sprayed the catalyst surface is dry, and the liquid reactant is fed as an atomized spray using a fine nozzle. The alternate wet and dry conditions are experienced by the catalyst surface during the reaction. Which is advantageous to the dehydrogenation reaction by maintaining the higher temperature so as to favour the dehydrogenation reaction, the rapid desorption of the aromatic products prevents reverse reaction, site blocking by aromatic products or further dissociation of the benzene leading to hydrogenolysis. Considering the above mentioned factors the highly selective dehydrogenation over Ni based catalyst may be explained.

For Ni catalyst promoted by addition of 0.5 wt% Pt, the activity was highest in terms of the hydrogen production rate and percentage conversion of the cyclohexane. The XRD patterns of the promoted catalyst has a small peak which can be assigned to Pt. The XRD patterns of catalysts with addition of higher

Table 2
Particle size of metal catalysts, dispersion and turn over frequency

Catalyst (wt%)	Average particle size by XRD (nm)	Average particle size by TEM (nm)	Dispersion[a] (%)	Turn over frequency[b] (s^{-1})
10% Ni	10	–	1.09	2.22
20% Ni	11	10	0.49	3.54
40% Ni	17	–	0.43	1.62
0.5% Pt	6	6	12.99	0.26
20% Ni + 0.5% Pt	10	9	0.69	4.10

[a]Estimated by H$_2$ chemisorption.
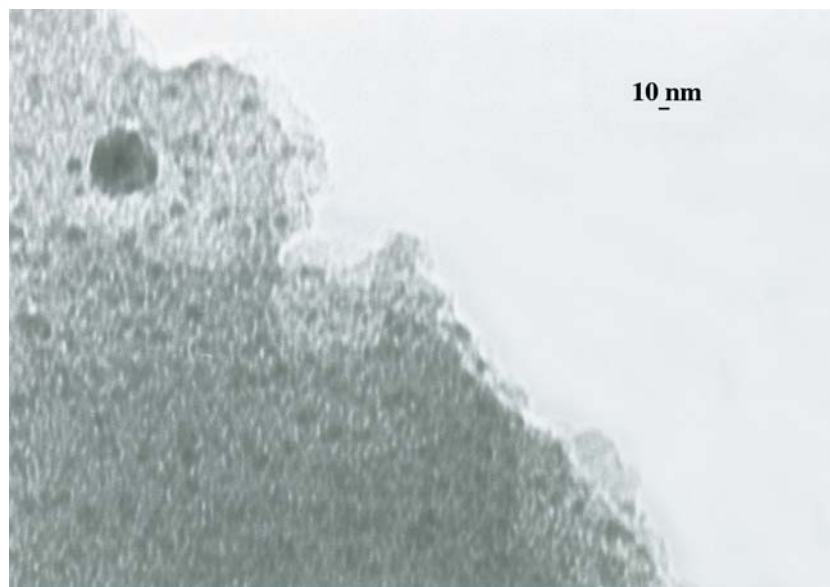[b]Calculated as number of molecules converted/number of surface atoms.

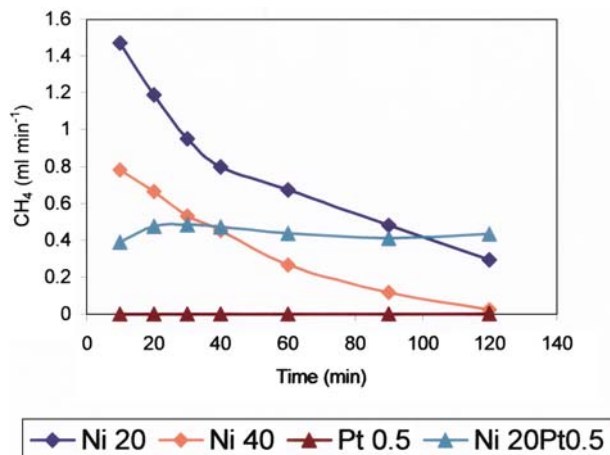Figure 4. TEM image of the Ni/ACC catalyst, 20 wt% Ni loading.

Figure 5. Methane flow rates at 300 °C over various catalysts supported on activated carbon cloth, cyclohexane feed rate 3.8 mmol min^{-1} (pulse of 0.128 mmol, 2 s intervals).

nation of cyclohexane is very promising for hydrogen storage and supply systems with non-noble metal catalysts. When Ni catalysts is promoted with a small amount of Pt, it exhibits good stability and a potential synergestic effect, which is excellent feature for minimizing the Pt content in the catalysts.

loading of Pt i.e. 5–20 wt% Ni catalyst was obtained to confirm the co-existence of the Ni and Pt on the carbon support. The promotion of catalytic activity by addition of a small amount of Pt to Ni based catalysts may be attributed to the easy formation of molecular hydrogen and rapid desorption of it due to the reverse spillover effect in the presence of Pt [11] in addition to the synergistic effect of Ni–Pt for C–H bond dissociation and abstraction of hydrogen [12,13]. Simultaneously Pt helps to keep the Ni in reduced state and thus maintains the activity during the reaction.

4. Conclusion

The stable monometallic Ni catalysts supported on carbon having high selectivity towards the dehydroge-

References

[1] P. Taube and M.A. Taube, Adv. Hydrogen Energy 2 (1981) 1077.
[2] S. Hodoshima, H. Arai and Y. Saito, Int. J. Hydrogen Energy 28 (2003) 197.
[3] S. Hodoshima, H. Arai, S. Takaiwa and Y. Saito, Int. J. Hydrogen Energy 28 (2003) 1255.
[4] N. Kariya, A. Fukuoka and M. Ichikawa, Appl. Catal. A: Gen. 233 (2002) 91.
[5] N. Kariya, A. Fukuoka, T. Utagawa, M. Sakuramoto, Y. Goto and M. Ichikawa, Appl. Catal. A: Gen. 247 (2003) 247.
[6] I. Kobayashi, K. Yamamoto and H. Kameyama, Chem. Eng. Sci. 54 (1999) 1319.
[7] J.H. Sinfelt, J.L. Carter and D.J.C. Yates, J. Catal. 24(2) (1972) 283.
[8] A. Onda, T. Komatsu and T. Yashima, J. Catal. 201 (2001) 13.
[9] R.B. Biniwale, A. Mizuno and M. Ichikawa, Appl. Catal. A: Gen. 276 (2004) 169.
[10] B.C. Gates, J.R. Katzer and G.C.A. Schuit, *Chemistry of Catalytic Processes* (McGraw-Hill Inc., New York, 1979) 264.
[11] M. Arai, M. Fukushima and Y. Nishiyama, Appl. Surf. Sci. 99 (1996) 145.
[12] A.H. Janowicz and R.G. Bergman, J. Am. Chem. Soc. 104 (1982) 352.
[13] J.K. Hoyano and W.A.G. Graham, J. Am. Chem. Soc. 104 (1982) 3772.