

# Rapid Hydrogenation of Toluene in a One-Pass Reactor at Ambient Temperature and Pressure on a Novel Nanostructured Super-Alloy Catalysts without Containing Noble Metals

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## Abstract

Novel Ni-Re super-alloy catalyst system is found for rapid hydrogenation of toluene to methylcyclohexane (MCH) in a one-pass reactor under mild reaction conditions. The novel bimetallic Ni-Re alloy catalysts exhibit the remarkably enhanced activity and stability for hydrogenation of toluene by comparison with monometallic Ni catalyst. The catalytic performance of novel Ni-Re catalyst is compared with that of Pt catalysts for hydrogenation of toluene. The better activity maintenance of the Ni-Re catalysts than the Pt-based catalysts are found. The alloying effect of Ni with Re is identified by XRD and EXAFS measurements.

**Keywords:** Liquid Organic Hydride; Hydrogenation of Toluene; Ni-Re Super-Alloy Catalysts

## Introduction

The hydrogenation of aromatics is an important reaction for the production of cyclohexane – an important precursor in the manufacturing of nylon-6,6 [1-3]. Hydrogen is a clean energy carrier and it can be generated from renewable energy including solar energy, wind energy, etc. The toluene/methylcyclohexane couple is a promising cyclic hydrocarbon combination for the safe and feasible storage of hydrogen [4]. In this method, hydrogen is fixed to toluene ( $C_7H_8$ ) with the hydrogenation reaction and converted into MCH ( $C_7H_{14}$ ) that is able to be transported with a chemical tanker as same as toluene. In the demand site, hydrogen is generated from MCH by dehydrogenation reaction, and toluene is recovered for the recycle use. Liquid organic hydrogen carrier (LOHC) is suitable for large-scale storage and long distance transportation due to the ambient condition with the low potential risk. Not only is the toluene/methylcyclohexane couple reversible and highly selective, but it is free from carcinogenic products. Furthermore, it has a relatively high hydrogen storage capacity (6.2 wt.%, 46.5 kg- $H_2$ /m<sup>3</sup>), and the volatility range of the constituents makes the couple compatible with existing transportation infrastructure, such as storage tanks and refueling stations, giving it an advantage over other solid hydrocarbons for hydrogen storage and transport [4-7]. However, the hydrogenation of aromatics, including toluene, is traditionally performed using elevated temperatures and pressures, which often exceed 100 °C and 50 atm  $H_2$  [8]. Thus, effecting the reduction under mild conditions is an important challenge in terms of energy conservation and associated environmental considerations. This is of particular concern when examining the suitability of the toluene/methylcyclohexane couple for the reversible storage of hydrogen, i.e. the system's usability in a decentralised transport infrastructure. Despite much research on the hydrogenation of toluene at mild temperature, elevated pressures are still required. Additionally, the catalysts are often with low activity and/or low stability [2]. A further approach to overcome the problems of stability has been to immobilise the nanoparticles on a solid support, such as silica, boehmite nanofibers, multi-walled carbon nanotubes, titanium dioxide, and others [1,2,9-11]. Recently, Özkar et al. reported the hydrogenation of aromatics at room temperature under 3 atm  $H_2$  using colloidal nanozeolite framework-stabilised ruthenium (0) nanoclusters, and obtained a turnover-frequency (TOF) of 1800 h<sup>-1</sup> for the hydrogenation of toluene. Although the hydrogenation of toluene and tetralin at ambient temperature and pressure in a batch reactor has been recently reported and 79% of toluene conversion was obtained, noble metal catalysts are necessary for the reaction [12]. Ni-Re based superalloy catalysts have been successfully applied to the steam reforming of gasoline to generate hydrogen [13-18]. In the present presentation, rapid hydrogenation of toluene in a one-pass reactor at ambient temperature and pressure on a novel super-alloy catalysts without containing noble metals are studied and compared with Pt-based catalysts.

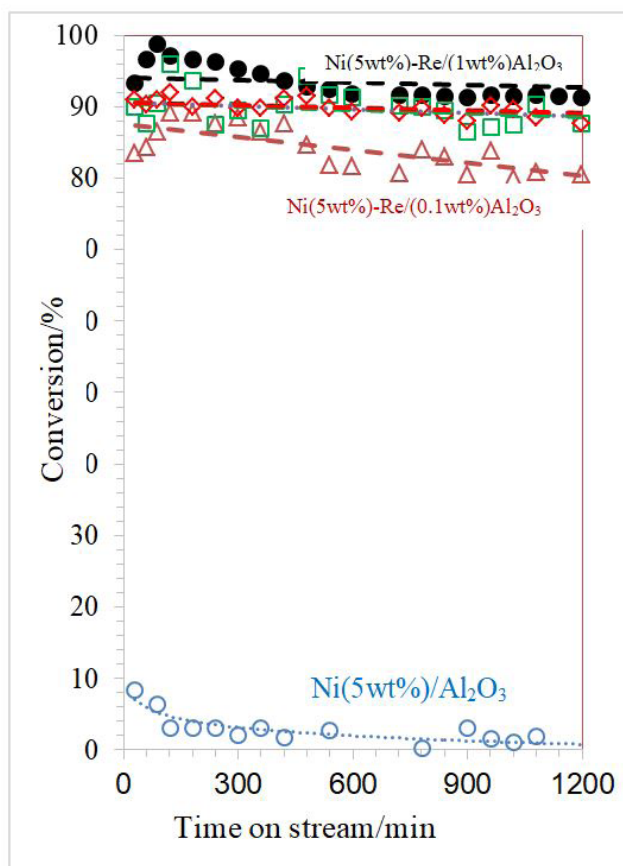
## Experimental

Ni/ $Al_2O_3$  and Pt/ $Al_2O_3$  catalysts were prepared by impregnating  $Al_2O_3$  with aqueous solution of  $Ni(NO_3)_2$  and  $Pt(NH_3)_4(NO_3)_2$  respectively at room temperature, followed by drying at 333 K for 4h and 393 K for 4h, calcination at 773 K for 4 h. Ni-Re/ $Al_2O_3$  was prepared by impregnating Ni/ $Al_2O_3$  with aqueous solution of  $NH_4ReO_4$  at room temperature, followed by drying at 333K for 4h and 393K for 4h, calcination at 773 K for 4 h. The catalytic tests for hydrogenation of toluene to MCH was conducted in a demonstration equipment with two reactors. The volume of each reactor is about 200 ml. The catalytic tests were also conducted in a fixed-bed one-pass flow smaller reactor. The low rates of toluene, MCH and hydrogen are controlled by mass-flow controllers. The products including MCH and toluene are condensed and collected in condenser at room temperature. All the collected products in the condenser were analyzed by gas chromatographs with a flame ionization detector (FID).

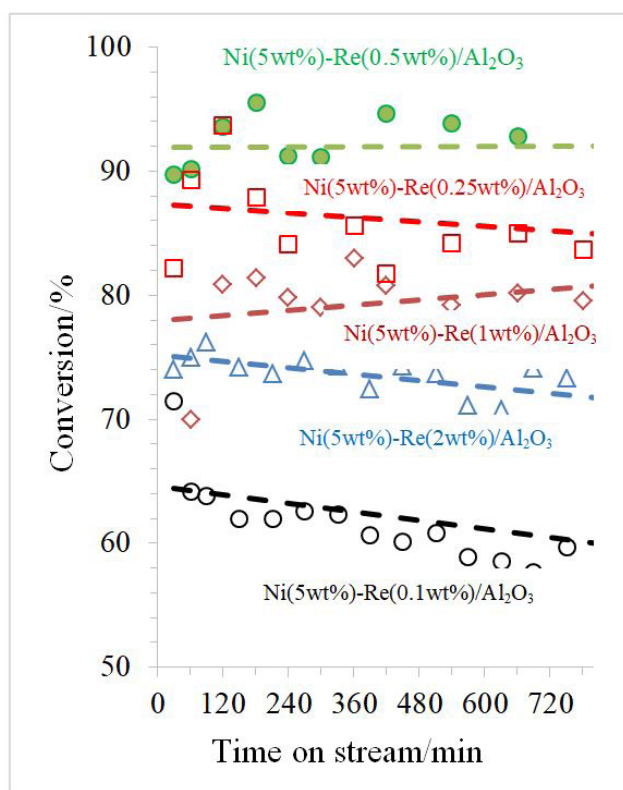
XRD patterns were recorded by using a Rigaku Ultima III diffractometer with Cu K $\alpha$  radiation ( $\lambda = 0.154178$ ) at 40 kV and 40 mA. The scanning angle ( $2\theta$ ) ranged from 5 to 50° at a scanning rate of 5° min<sup>-1</sup>.

## Results and Discussion

Figure 1 shows conversions with time on stream for hydrogenation of toluene on Ni(5wt%)/ $Al_2O_3$  and Ni(5wt%)-Re/ $Al_2O_3$  with different Re loadings at 393K and toluene WSV of 3.4h<sup>-1</sup> and  $H_2$ /Toluene/ $N_2$  mole ratio of =3.8/1/0.6.



**Figure 1:** Conversions with time on stream for hydrogenation of toluene on Ni(5wt%)/Al<sub>2</sub>O<sub>3</sub> and Ni(5wt%)-Re/Al<sub>2</sub>O<sub>3</sub> with different Re loadings at 393 K and toluene WSV of 3.4 h<sup>-1</sup> and H<sub>2</sub>/Toluene/N<sub>2</sub> mole ratio of =3.8/1/0.6



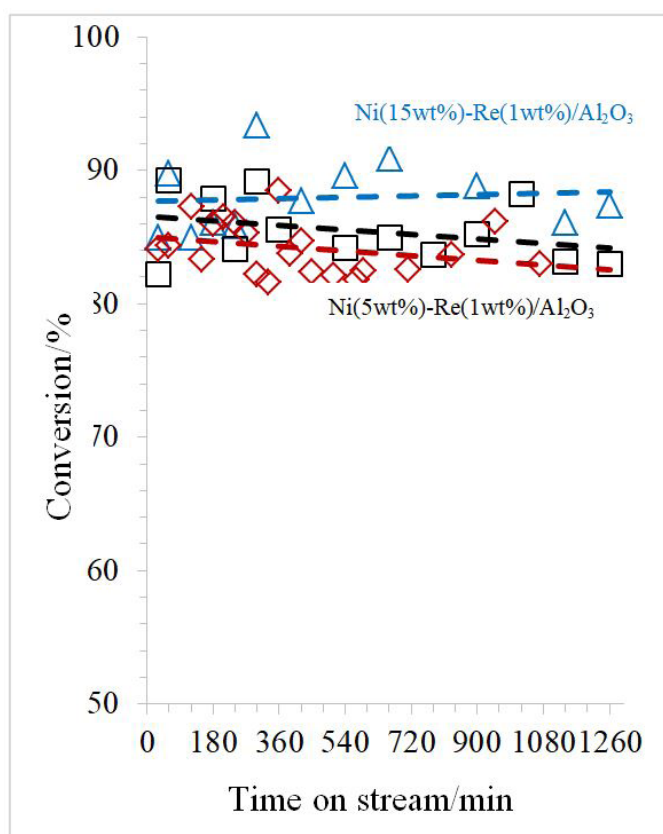
**Figure 2:** Catalytic performance of Ni(5wt%)-Re/Al<sub>2</sub>O<sub>3</sub> catalysts with different Re loadings for hydrogenation of toluene at 393 K and toluene WSV of 5.9 h<sup>-1</sup> and H<sub>2</sub>/Toluene/N<sub>2</sub> mole ratio of =3.8/1/0.6

We can see from Figure 1 that the initial conversion for toluene hydrogenation on Ni(5wt%)/Al<sub>2</sub>O<sub>3</sub> is about 10% and the conversion is declined to zero after about 20 hours of time on stream. The initial toluene conversion on Ni(5wt%)Re(0.1wt%)/Al<sub>2</sub>O<sub>3</sub> is about 88% and it is declined to about 80% after about 20 hours of time on stream, which is about 8 time higher than that on Ni(5wt%)/Al<sub>2</sub>O<sub>3</sub> catalyst. The initial toluene conversions on Ni(5wt%)Re(0.25wt%)/Al<sub>2</sub>O<sub>3</sub> and Ni(5wt%)Re(0.5wt%)/Al<sub>2</sub>O<sub>3</sub> catalysts are about 90% and they are stable during about 20 hours of time on stream. The initial maximum toluene conversion on Ni(5wt%)Re(1wt%)/Al<sub>2</sub>O<sub>3</sub> is about 98% and it is declined to about 93% after about 20 hours of time on stream. Therefore the activity of Ni(5wt%)/Al<sub>2</sub>O<sub>3</sub> is remarkably enhanced by addition of about only 0.1wt% Re. The activity of Ni(5wt%)-Re/Al<sub>2</sub>O<sub>3</sub> is increased further with increasing Re loadings from 0.1wt% to 1wt% for toluene hydrogenation under the reaction conditions. Catalytic activities of Ni(5wt%)-Re/Al<sub>2</sub>O<sub>3</sub> catalysts with different Re loadings of from 0.1wt% to 2wt% are compared further for hydrogenation of toluene at 393 K and a higher toluene WSV of 5.9 h<sup>-1</sup> and H<sub>2</sub>/Toluene/N<sub>2</sub> mole ratio of =3.8/1/0.6 as shown in Figure 2.

In the higher toluene WSV of 5.9 h<sup>-1</sup>, the activity variation of catalysts with different Re loadings from 0.1wt% to 2wt% are more evident than that at a lower WSV of 3.4 h<sup>-1</sup>. The catalytic activity order for toluene hydrogenation of the Ni(5wt%)-Re/Al<sub>2</sub>O<sub>3</sub> catalysts with different Re loadings from 0.1wt% to 2wt% is as follows, Ni(5wt%)Re(0.1wt%)/Al<sub>2</sub>O<sub>3</sub> > Ni(5wt%)Re(0.25wt%)/Al<sub>2</sub>O<sub>3</sub> > Ni(5wt%)Re(0.5wt%)/Al<sub>2</sub>O<sub>3</sub> > Ni(5wt%)Re(1wt%)/Al<sub>2</sub>O<sub>3</sub> > Ni(5wt%)Re(2wt%)/Al<sub>2</sub>O<sub>3</sub>.

The toluene conversion on Ni(5wt%)-Re/Al<sub>2</sub>O<sub>3</sub> catalysts is increased with increasing Re loadings from 0.1wt% to 0.5wt% and toluene conversion on Ni(5wt%)-Re/Al<sub>2</sub>O<sub>3</sub> catalysts is decreased with increasing Re loadings from 0.5wt% to 2wt% as shown in Figure 2.

Toluene conversions with time on stream on Ni(5wt%)-Re(1wt%)/Al<sub>2</sub>O<sub>3</sub>, Ni(10wt%)-Re(1wt%)/Al<sub>2</sub>O<sub>3</sub> and Ni(15wt%)-Re(1wt%)/Al<sub>2</sub>O<sub>3</sub> catalysts with different Re-loadings for hydrogenation of toluene at 393K and toluene WSV of 5.9h<sup>-1</sup> and H<sub>2</sub>/Toluene/N<sub>2</sub> mole ratio of =3.8/1/0.6 are shown in Figure 3.



**Figure 3:** Toluene conversion on Ni-Re(1wt%)/Al<sub>2</sub>O<sub>3</sub> with different Ni loadings at 393 K and toluene WSV of 5.9 h<sup>-1</sup> and H<sub>2</sub>/toluene/N<sub>2</sub> mole ratio of 3.8/1/0.6

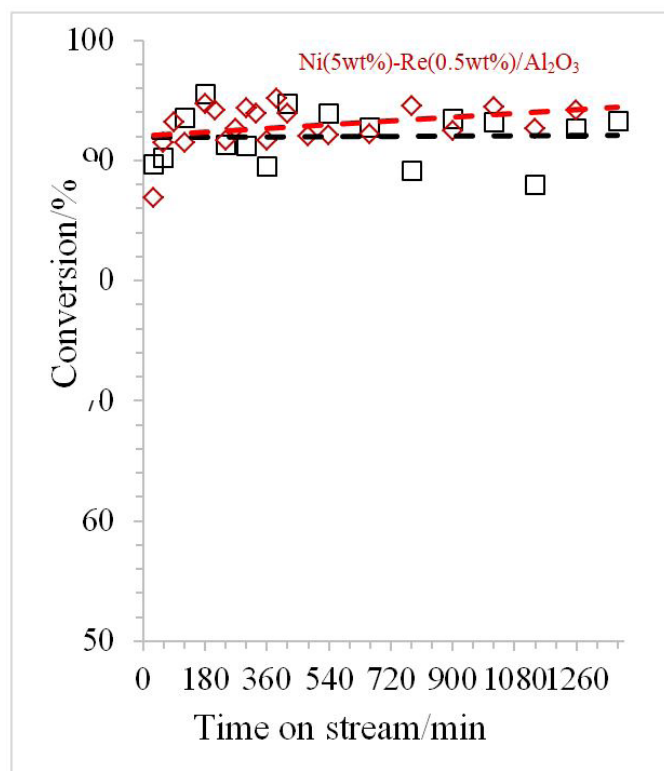
We can see from Figure 3 that the toluene conversions with time on stream on Ni(5wt%)-Re(1wt%)/Al<sub>2</sub>O<sub>3</sub> and Ni(10wt%)-Re(1wt%)/Al<sub>2</sub>O<sub>3</sub> are similar and they are about 85% under the reaction conditions. The toluene conversion on Ni(15wt%)-Re(1wt%)/Al<sub>2</sub>O<sub>3</sub> is 88%, which is about 3% higher than that on Ni(5wt%)-Re(1wt%)/Al<sub>2</sub>O<sub>3</sub> and Ni(10wt%)-Re(1wt%)/Al<sub>2</sub>O<sub>3</sub>. These indicate that the catalyst activity almost has no increase by increasing Ni-loading from 5 wt% to 10 wt% and it has a little increase by increasing Ni-loading from 10 wt% to 15 wt% as shown in Figure 3. Therefore the activity of the Ni/Al<sub>2</sub>O<sub>3</sub> for hydrogenation of toluene is remarkably enhanced by alloying of Ni with Re to form the new alloy active sites. The higher Ni-loadings or higher Re-loadings are not necessary for the high activities of the catalysts. The suitable Ni-loading is about 5wt% and the suitable Re loading is about 0.25-0.5 wt% for obtaining the best catalytic performance of Ni-Re/Al<sub>2</sub>O<sub>3</sub> catalysts for hydrogenation of toluene.

Catalyst	WHSV	Conv.	Sel.
Ni(10wt%)Re(0.5wt%)	2.1 h <sup>-1</sup>	99.0%	99.9%
Ni(20wt%)Re(1wt.)	2.1 h <sup>-1</sup>	99.5%	99.9%
Ni(20wt%)Re(1wt.)	1.6 h <sup>-1</sup>	99.8%	99.9%

T=393 K; Toluene/H<sub>2</sub>=1/5; P= atmospheric pressure

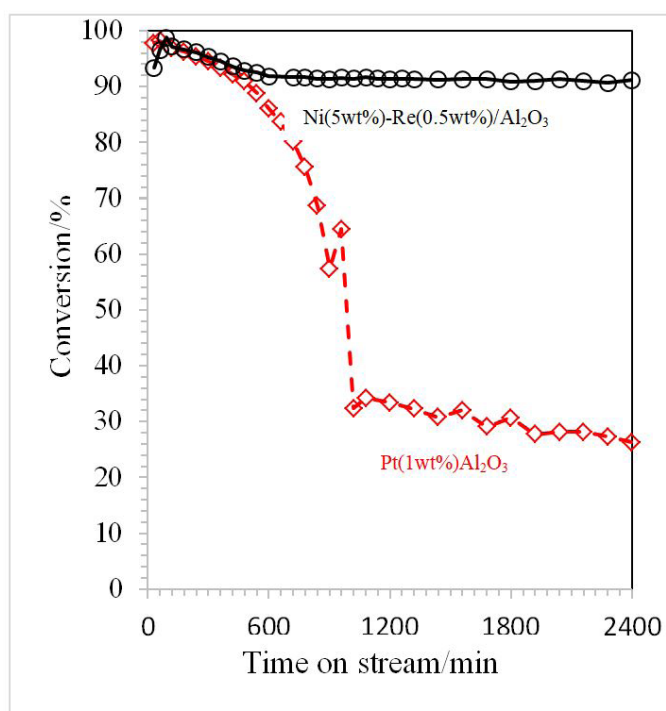
**Table 1:** Conversion and selectivity of toluene hydrogenation on Ni-Re/Al<sub>2</sub>O<sub>3</sub> catalysts with the different compositions

The dependence of conversion and selectivity on the composition of Ni-Re/Al<sub>2</sub>O<sub>3</sub> is further studied in Table 1. We can see from Table 1 that a high toluene conversion of about 99.8% with a high selectivity of about 99.9% attained on Ni-Re/Al<sub>2</sub>O<sub>3</sub> catalyst. In order to collect the relatively higher purity liquid product by condensation in one step, the high conversion of up to 100% is highly desired for hydrogen storage by one pass flow hydrogenation of toluene.



**Figure 4:** Toluene conversions on Pt(1wt%)/Al<sub>2</sub>O<sub>3</sub> and Ni(5wt%)-Re(0.5wt%)/Al<sub>2</sub>O<sub>3</sub> catalysts for hydrogenation of toluene at 393 K and toluene WSV of 5.9 h<sup>-1</sup> and H<sub>2</sub>/Toluene/N<sub>2</sub> mole ratio of =3.8/1/0.6

It has been well known that Pt has been the best element as the active component of the catalysts for hydrogenation of unsaturated hydrocarbons and dehydrogenation of saturated hydrocarbons. However the Pt is high cost noble element. It is highly desirable if we could find the other catalyst materials to instead of Pt catalysts for hydrogenation or dehydrogenation reactions. Figure 4 shows the toluene conversions with time on stream on Pt(1wt%)Al<sub>2</sub>O<sub>3</sub> and Ni(5wt%)-Re(0.5wt%)/Al<sub>2</sub>O<sub>3</sub> catalysts for hydrogenation of toluene at 393K and toluene WSV of 5.9 h<sup>-1</sup> and H /toluene/N<sub>2</sub> mole ratio of 3.8/1/0.6. The initial toluene conversion on Ni(5wt%)-Re(0.5wt%)/Al<sub>2</sub>O<sub>3</sub> is about 91% and it is quite stable with time on stream, which is quite similar to the toluene conversion on Pt(1wt%)Al<sub>2</sub>O<sub>3</sub> catalyst for toluene hydrogenation at 393K and toluene WSV of 5.9 h<sup>-1</sup> and H / toluene/N<sub>2</sub> mole ratio of 3.8/1/0.6 as shown in Figure 4.

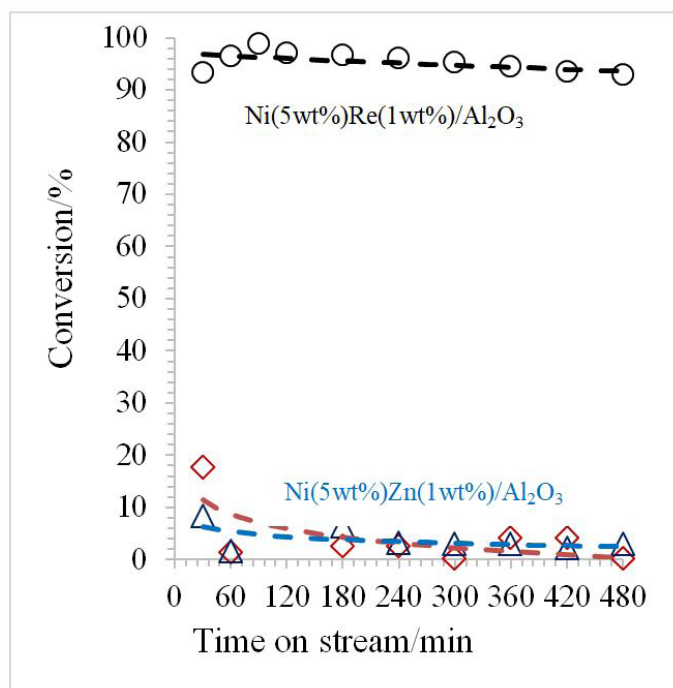


**Figure 5:** Toluene conversions with time on stream on Pt(1wt%)Al<sub>2</sub>O<sub>3</sub> and Ni(5wt%)-Re(0.5wt%)/Al<sub>2</sub>O<sub>3</sub> catalysts for hydrogenation of toluene at 393 K and toluene WSV of 3.4 h<sup>-1</sup> and H /Toluene/N<sub>2</sub> mole ratio of =3.8/1/0.6

Figure 5 shows the toluene conversions with time on stream on Pt(1wt%)Al<sub>2</sub>O<sub>3</sub> and Ni(5wt%)-Re(0.5wt%)/Al<sub>2</sub>O<sub>3</sub> catalysts for hydrogenation of toluene at 393 K and a lower toluene WSV of 3.4 h<sup>-1</sup> and H /Toluene/N<sub>2</sub> mole ratio of =3.8/1/0.6 during a longer time of about 20 hours on stream.

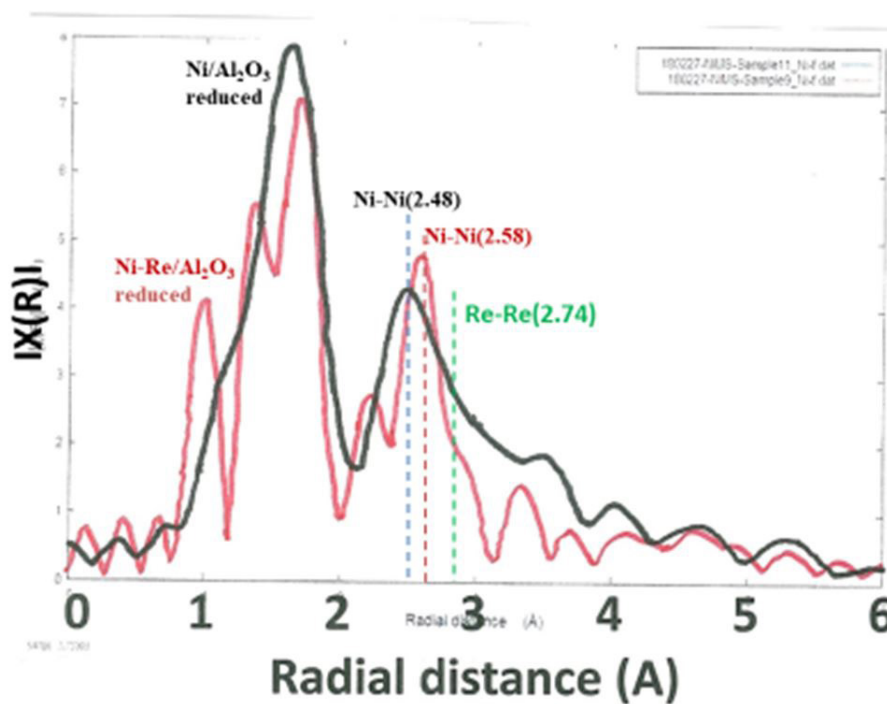
A high initial toluene conversion of over 99% is obtained on both Pt(1wt%)Al<sub>2</sub>O<sub>3</sub> and Ni(5wt%)-Re(0.5wt%)/Al<sub>2</sub>O<sub>3</sub> catalysts for hydrogenation of toluene at 393 K and a lower toluene WSV of 3.4 h<sup>-1</sup> and H /toluene/N<sub>2</sub> mole ratio of =3.8/1/0.6. The conversion of toluene hydrogenation is declined from over 99% to 20-30% after about 20 hours of time on stream on Pt(1wt%)Al<sub>2</sub>O<sub>3</sub> catalyst. The conversion of toluene hydrogenation is still maintained at over 92% after about 20 hours of time on stream on the Ni(5wt%)-Re(0.5wt%)/Al<sub>2</sub>O<sub>3</sub> catalyst for hydrogenation of toluene at 393 K and a lower toluene WSV of 3.4 h<sup>-1</sup> and H /toluene/N<sub>2</sub> mole ratio of =3.8/1/0.6. as shown in Figure 5. Therefore the Ni(5wt%)-Re(0.5wt%)/Al<sub>2</sub>O<sub>3</sub> catalyst exhibit the much better activity maintenance at the high toluene conversion than the Pt(1wt%)Al<sub>2</sub>O<sub>3</sub> catalyst for hydrogenation of toluene at 393K and toluene WSV of 3.4 h<sup>-1</sup> and H /Toluene/N<sub>2</sub> mole ratio of =3.8/1/0.6. It is of significance that our developed novel Ni-Re alloy catalyst exhibits the similar activity to that of the Pt catalyst and the activity maintenance Ni-Re catalyst is much better than that of Pt catalyst for hydrogenation of toluene at high toluene conversion. Figure 6 shows comparison of Ni(5wt%)Re(1wt%)/Al<sub>2</sub>O<sub>3</sub> catalyst with other alloys such as Ni(5wt%)Zn(1wt%)/Al<sub>2</sub>O<sub>3</sub> and Ni(5wt%)V(1wt%)/Al<sub>2</sub>O<sub>3</sub> catalysts for hydrogenation of toluene at 393 K and toluene WSV of 3.4 h<sup>-1</sup> and H /toluene/N<sub>2</sub> mole ratio of =3.8/1/0.6.





**Figure 6:** Conversions of toluene with time on stream on Ni(5wt%)Re(1wt%)/Al<sub>2</sub>O<sub>3</sub>, Ni(5wt%)Zn(1wt%)/Al<sub>2</sub>O<sub>3</sub> and Ni(5wt%)V(1wt%)/Al<sub>2</sub>O<sub>3</sub> catalysts at 393 K and toluene WSV of 3.4 h<sup>-1</sup> and H<sub>2</sub>/toluene/N<sub>2</sub> mole ratio of =3.8/1/0.6

We can see from Figure 6 that the Ni(5wt%)Zn(1wt%)/Al<sub>2</sub>O<sub>3</sub> and Ni(5wt%)V(1wt%)/Al<sub>2</sub>O<sub>3</sub> alloy catalysts exhibit the much lower activity than the Ni(5wt%)Re(1wt%)/Al<sub>2</sub>O<sub>3</sub> catalyst for hydrogenation of toluene at 393K and toluene WSV of 3.4h<sup>-1</sup> and H<sub>2</sub>/toluene/N<sub>2</sub> mole ratio of =3.8/1/0.6 as shown in Figure 6. The alloying effect of Ni with Re on the structure of Ni nanoparticles is characterized by EXAFS and obtained XRD and the EXAFS and XRD results are shown in Figures 7 and 8. Figure 8 compared



**Figure 7:** EXAFS profiles of Ni(5wt%)/Al<sub>2</sub>O<sub>3</sub> and Ni(5wt%)-Re(1wt%)/Al<sub>2</sub>O<sub>3</sub> samples after reaction

the EXAFS profiles of Ni(5wt%)/Al<sub>2</sub>O<sub>3</sub> and Ni(5wt%)-Re(1wt%)/Al<sub>2</sub>O<sub>3</sub> samples after reaction of toluene hydrogenation. We can see from Figure 7 that the Ni-Ni bond length on Ni(5wt%)-Re(1wt%)/Al<sub>2</sub>O<sub>3</sub> is about 0.258 nanometer and the Ni-Ni bond length on Ni(5wt%)/Al<sub>2</sub>O<sub>3</sub> sample is about 0.248 nanometer. The Ni-Ni bond length on Ni(5wt%)-Re(1wt%)/Al<sub>2</sub>O<sub>3</sub> sample is about 0.01nanometer longer than that on Ni(5wt%)/Al<sub>2</sub>O<sub>3</sub> sample. The alloying of Ni with Re lead to the expanding of the Ni-Ni bonds in the Ni-Re alloy nanoparticles. Expanding of Ni-Ni bond length in the Ni-Re alloy nanoparticles is the reason why the bimetallic Ni-Re alloy nanoparticles are much more active than the monometallic Ni nanoparticles for catalyzing the hydrogenation of toluene.

The alloying effect of Ni with Re on the structure Ni-Re/Al<sub>2</sub>O<sub>3</sub> catalyst is also characterized by XRD. The XRD patterns of Al<sub>2</sub>O<sub>3</sub>, Ni(5wt%)/Al<sub>2</sub>O<sub>3</sub>, Ni(5wt%)-Re(0.1wt%)/Al<sub>2</sub>O<sub>3</sub>, Ni(5wt%)-Re(0.25wt%)/Al<sub>2</sub>O<sub>3</sub>, Ni(5wt%)-Re(0.5wt%)/Al<sub>2</sub>O<sub>3</sub>, Ni(5wt%)-Re(1wt%)/Al<sub>2</sub>O<sub>3</sub> and Ni(5wt%)-Re(2wt%)/Al<sub>2</sub>O<sub>3</sub> samples after reduction by flowing hydrogen at 703K for 1h are shown in Figure 8.

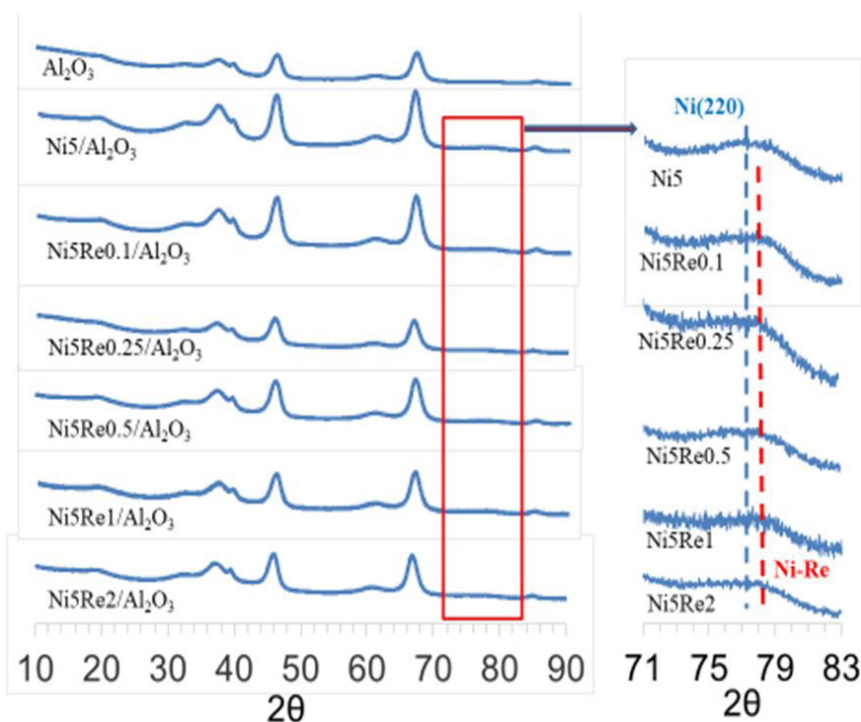


Figure 8: XRD patterns of Al<sub>2</sub>O<sub>3</sub>, Ni/Al<sub>2</sub>O<sub>3</sub> and Ni(5wt%)-Re/Al<sub>2</sub>O<sub>3</sub> with different Re-loadings

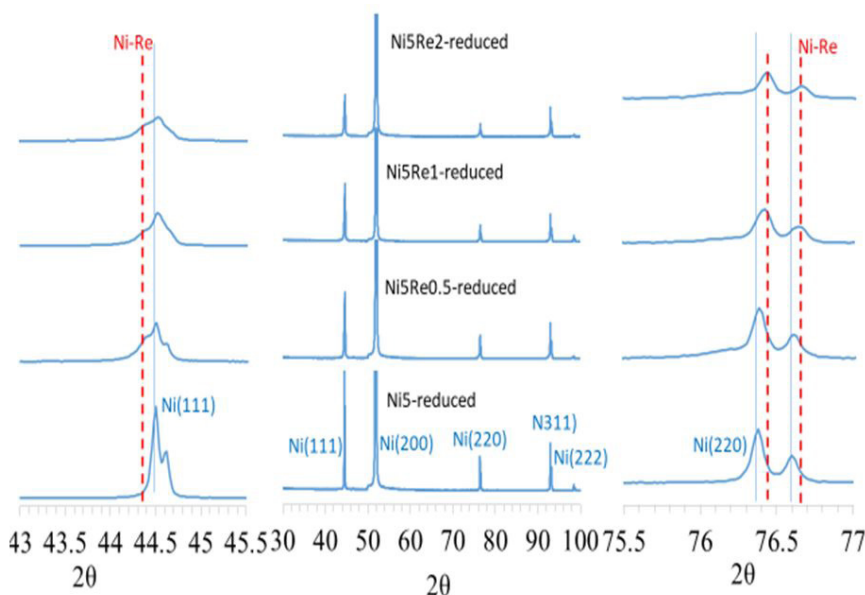


Figure 9: Alloying effect of Ni with Re on the surface of Ni film characterized by XRD



Since the Ni(111) and Ni(200) XRD peaks of Ni(5wt%)/Al<sub>2</sub>O<sub>3</sub>, Ni(5wt%)-Re(0.1wt%)/Al<sub>2</sub>O<sub>3</sub>, Ni(5wt%)-Re(0.25wt%)/Al<sub>2</sub>O<sub>3</sub>, Ni(5wt%)-Re(0.5wt%)/Al<sub>2</sub>O<sub>3</sub>, Ni(5wt%)-Re(1wt%)/Al<sub>2</sub>O<sub>3</sub> and Ni(5wt%)-Re(2wt%)/Al<sub>2</sub>O<sub>3</sub> samples are overlaid with the XRD peaks of Al<sub>2</sub>O<sub>3</sub> substrate (support), the Ni(220) XRD peaks of Ni(5wt%)/Al<sub>2</sub>O<sub>3</sub>, Ni(5wt%)-Re(0.1wt%)/Al<sub>2</sub>O<sub>3</sub>, Ni(5wt%)-Re(0.25wt%)/Al<sub>2</sub>O<sub>3</sub>, Ni(5wt%)-Re(0.5wt%)/Al<sub>2</sub>O<sub>3</sub>, Ni(5wt%)-Re(1wt%)/Al<sub>2</sub>O<sub>3</sub> and Ni(5wt%)-Re(2wt%)/Al<sub>2</sub>O<sub>3</sub> samples are compared in the 2θ range of 71-83 degree although the Ni(220) peak is relatively more weak than the Ni(111) peak or Ni(200) peak. We can see from Fig 8 that the 2θ angle of Ni (220) peak in the Ni(5wt%)-Re(0.1wt%)/Al<sub>2</sub>O<sub>3</sub>, Ni(5wt%)-Re(0.25wt%)/Al<sub>2</sub>O<sub>3</sub>, Ni(5wt%)-Re(0.5wt%)/Al<sub>2</sub>O<sub>3</sub>, Ni(5wt%)-Re(1wt%)/Al<sub>2</sub>O<sub>3</sub> and Ni(5wt%)-Re(2wt%)/Al<sub>2</sub>O<sub>3</sub> samples are shifted to the higher value by comparison with that of Ni(5wt%)/Al<sub>2</sub>O<sub>3</sub> sample because of the alloying effect of Ni with Re.

In order to observe the alloying effect of Ni with Re more clearly by XRD, Ni(5wt%)/Ni-foil, Ni(5wt%)-Re(0.5wt%)/Ni-foil, Ni(5wt%)-Re(1wt%)/Ni-foil, Ni(5wt%)-Re(2wt%)/Ni-foil, samples are prepared by using Ni-foil as substrate instead of Al<sub>2</sub>O<sub>3</sub>. The XRD patterns of the Ni(5wt%)/Ni-foil, Ni(5wt%)-Re(0.5wt%)/Ni-foil, Ni(5wt%)-Re(1wt%)/Ni-foil and Ni(5wt%)-Re(2wt%)/Ni-foil samples after reduction by following hydrogen at 553K for 1h are compared in Figure 9. I can clearly see that the Ni(111) peak of Ni-Re samples is shifted to the lower 2θ angle values and Ni(220) peak shifted to the higher 2θ values by comparison with the Ni(111) and Ni(220) peaks of Ni sample. The XRD results in Figure 9 confidently prove the alloying effect of Ni with Re in the Ni-Re catalysts.

## Conclusions

A novel bimetallic Ni-Re alloy nanoparticles catalyst system is found for highly efficient hydrogenation of toluene to methylcyclohexane. The alloying effect of Ni with Re lead to the 2θ angle of Ni(220) XRD peak being shifted to the higher value and a new XRD peak at 2θ angle of about 44.3 degree is appeared near the Ni(111) peak at the 2θ angle of about 44.5 degree. Bond length expanding of Ni-Ni resulted from the alloying effect of Ni with Re is identified by EXAFS measurements.

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