Hydrodechlorination of trichloroethylene over Pd/NiMgAlO catalysts: Effect of support composition

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Introduction

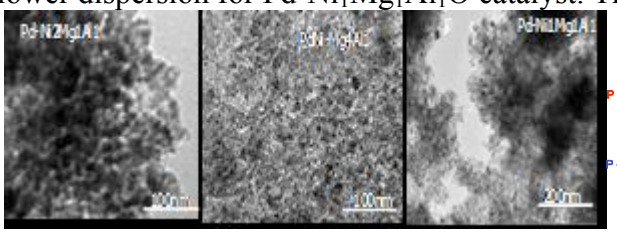
Organo-halogenated compounds are hazardous pollutants that are widely distributed in all parts of the world. Trichloroethylene (TCE) although has a wide application it is regarded as an environmental pollutant due to it low-degradability and high toxicity. Of the different treatment methodologies, catalytic hydrodechlorination (HDCl) is the promising non-destructive technique that transforms TCE pollutants into non-toxic or useful raw material (ethylene or ethane) [1,2]. Supported metals like palladium have shown a good catalytic activity towards this reaction. Similar to Cu-hydrotalcite [3], Ni-hydrotalcite derived mixed oxide (NiMgAlO) supports can be candidate for this type reaction. In the support, Ni can involve directly in HDCl reaction [1,3] while Mg increases the basicty of the support leading to higher catalytic activity. Based on this, the objective of this work is preparation of a series of Pd-NiMgAlO (with different Ni, Mg, Al molar ratio) catalysts for gas-phase hydrodechlorination of trichloroethylene to more valuable product, ethylene instead of ethane.

Experimental

The hydrotalcite-like compound was prepared by traditional co-precipitation of $Ni(NO_3)_2.6H_2O$, $Mg(NO_3)_2.6H_2O$ and $Al(NO_3)_3.9H_2O$ with NaOH. After calcinations, three different mixed oxides with different molar proportions were obtained: $Ni_2Mg_1Al_1O$, $Ni_1Mg_1A1_1O$, and $Ni_1Mg_4Al_1O$. The mixed oxides were then impregnated by an ethanol solution of $Pd(Ac)_2$ (Pd =0.5 wt/wt %). The catalyst was dried and finally calcined at 573K for 2 hours and named as Pd-$Ni_2Mg_1Al_1O$ and so on. The catalysts were characterized by XRD, TPR, BET, H_2-chemisorption, TEM and CO-FTIR. Gas-phase hydrodechlorination trichloroethylene was studied in a fixed-bed flow tubular reactor using 0.10 g of catalyst at atmospheric pressure and temperature of 573K. H2/TCE molar ratio was maintained to its stiochiometric value.

Results and discussion

The XRD patterns of the prepared catalysts are characteristic of well-defined crystallized mixed oxide with NiO structure & no distinct peaks of PdO species was observed. Pd-$Ni_2Mg_1Al_1O$, Pd-NiMgAlO, and Pd-$NiMg_4AlO$ TEM images however showed a uniformly distributed palladium particles with average particle size of correspond to 4.52nm, 4nm and 6nm respectively as shown in fig1. Fig 2 shows CO-FTIR spectra of prepared catalysts. The FTIR band b/n 2122-2000 nm represent for linear carbonyls bonded with Pd (or Pd-Ni). The high intensity of this peak in Pd-$Ni_2Mg_1Al_1O$ catalyst signifies a higher dispersion of Pd than Pd-$Ni_1Mg_1Al_1O$ catalyst. The broad peaks b/n 2000-1800 nm represent for bridged carbonyls, which represent lower dispersion for Pd-$Ni_1Mg_1Al_1O$ catalyst. The HDCl catalytic activity vs. time of



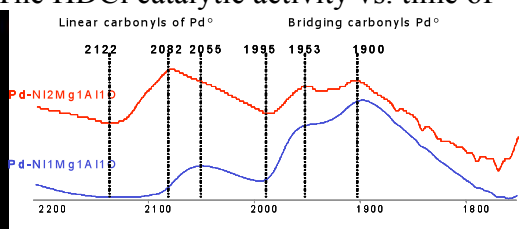


Figure 1. TEM images of the catalysts

reaction is shown in Fig 3. Ni_2Mg_1AlO support is associated with 20% of TCE conversion while introduction of Pd (0.5%), in Pd-Ni_2Mg_1AlO catalyst, leads to nearly complete HDCl activity [1]. Pd-$Ni_1Mg_1Al_1O$ catalyst presents the lowest catalytic activity (60%). Increasing the basicity of the support favors the HDCl activity as shown for Pd-$Ni_1Mg_4Al_1O$ catalyst (>90%). In general, these catalysts are characterized by good stability. The main products formed are ethane and ethylene as shown in Fig 4. Even though Pd-$Ni_1Mg_1Al_1O$ catalyst is associated with low activity it results in higher selectivity (>90%) to ethylene. Catalyst with higher HDCl activity favors ethane production than ethylene.

Figure 2. CO-FT-IR spectra

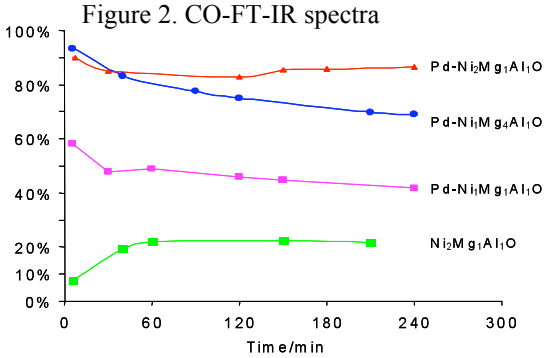


Figure 3. Catalytic activity of Pd/NiMgAlO

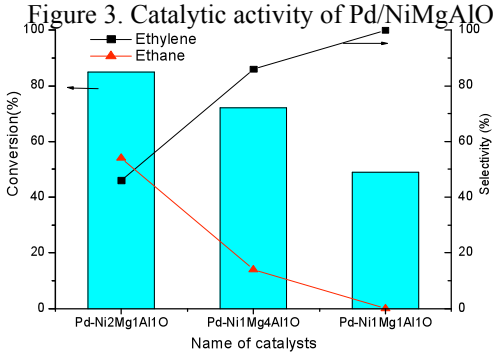


Figure 4- Selectivity and conversion at 3rd h

Conclusions

In conclusion, we have prepared a series of Pd-NiMgAlO catalysts with good performance towards catalytic HDCl of TCE. It is demonstrated that complete transformation of TCE to ethylene was observed for Pd-$Ni_1Mg_1Al_1O$ catalyst. High HDCl activity is favored by increasing basicity and Ni content of the support but inhibits ethylene production.

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