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 its 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 basicity 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(NO₃)₂.6H₂O, Mg(NO₃)₂.6H₂O and Al(NO₃)₃.9H₂O with NaOH. After calcinations, three different mixed oxides with different molar proportions were obtained: Ni₂Mg₆Al₄O₁₉, Ni₅Mg₄Al₁O, and Ni₄Mg₄Al₁O. 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-Ni₂Mg₆Al₄O and so on. The catalysts were characterized by XRD, TPR, BET, H₂-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-Ni₂Mg₆Al₄O, Pd-NiMgAlO, and Pd-NiMg₄AlO 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-Ni₂Mg₆Al₄O catalyst signifies a higher dispersion of Pd than Pd-Ni₅Mg₄Al₁O catalyst. The broad peaks b/n 2000-1800 nm represent for bridged carbonyls, which represent lower dispersion for Pd-Ni₄Mg₄Al₁O catalyst. The HDCl catalytic activity vs. time of
Figure 1: TEM images of the catalysts

reaction is shown in Fig 3. Ni$_2$Mg$_1$AlO support is associated with 20% of TCE conversion while introduction of Pd$_{0.5}$ in Pd-Ni$_2$Mg$_1$AlO catalyst, leads to nearly complete HDCI activity [1]. Pd$_{0.5}$ Ni$_1$Mg$_1$Al$_1$O catalyst presents the lowest catalytic activity (60%). Increasing the basicity of the support favors the HDCI activity as shown for Pd-Ni$_1$Mg$_4$Al$_1$O 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$_1$Mg$_1$Al$_1$O catalyst is associated with low activity it results in higher selectivity (>90%) to ethylene. Catalyst with higher HDCI activity favors ethane production than ethylene.

Conclusions

In conclusion, we have prepared a series of Pd-NiMgAlO catalysts with good performance towards catalytic HDCI of TCE. It is demonstrated that complete transformation of TCE to ethylene was observed for Pd-Ni$_1$Mg$_1$Al$_1$O catalyst. High HDCI activity is favored by increasing basicity and Ni content of the support but inhibits ethylene production.

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References

