Characterization of Cu-Au, Ni-Au bimetallic catalysts by TOF-SIMS and SEM-EDS techniques

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Introduction

Despite of intensive research efforts the nature of catalytic system supported on chromium-aluminum bioxide is relatively little known [1-3]. The main goal of this work was the determination of main physicochemical properties of gold doped nickel and copper catalysts supported on binary oxide $CrAl_3O_6$.

This paper is focused upon two subjects. First, the influence of support kind (co-precipitated bioxide Al_3CrO_6), and second, the effect of Au addition on the reduction behavior and catalytic properties of bimetallic Ni-Au Cu-Au supported catalysts in partial oxidation of methane POM and methanol synthesis MS. During last years gold was used mainly for low temperature processes such as CO and HC deep oxidation. However in the literature there is no information referring to gold doped nickel or copper catalysts.

Characterization of bimetallic Ni – Au, Cu-Au catalytic systems by TOF-SIMS and SEM – EDS techniques were carried out. The formation of alloy between copper and gold, as well as nickel and gold was experimentally proved. The promoting effect on catalytic activity and stability of gold addition was observed.

The evidence of alloying of copper and second metal was observed both during catalyst reduction as well as after reaction. The promoting effect of noble metal to copper catalyst was noticed. Modification by gold or silver improves catalyst activity up to ten times.

Materials and Methods

Catalysts were prepared by wet aqueous impregnation method. To prepare support precursors chromium and aluminum nitrates were used. The ammonia co-precipitated mixture of chromium and aluminum hydroxides with molar ratio Cr : Al = 1 : 3 were dried and calcined for 3h in air at 400°C. The obtained material represents binary oxide structure $CrAl_3O_6$. Metal phases (Ni, Cu, Au) were introduced on support surface by wet impregnation method with an aqueous solution of their nitrates and then the supported catalysts were dried and finally calcined 4h in air at 400°C. The metal loading was (1, 5)% Au – 20%Cu/$CrAl_3O_6$ or 2%Au-5%Ni/$CrAl_3O_6$

The catalysts were characterized by $TPD_{(CO,\ CO2,\ O2)}$, $TPRH_2$, low - temperature N_2 adsorption, TG-DTA-MS, SEM-EDS, TOF-SIMS and XRD methods. Catalytic activity tests were determined in POM and MS reactions were carried out in flow quartz reactors or gradientless reactor.

Results and Discussion

Specific surface area of binary oxide ($CrAl_3O_6$) supported catalyst was in the range 110-130 m^2/g . TPR studies carried out for Ni and Cu catalysts before and after gold promotion show rather no significant influence on TPR profiles. In the case of nickel catalysts there were observed two peaks (reduction of nickel chromite and superficial Cr^{6+} species) for copper catalysts there were observed two reduction effects (first connected to the CuO reduction, second to the copper chromate reduction). Phase composition measurements confirm the formation of above mentioned compounds during calcination process. Gold seems to occur in free metallic state on oxidic form of catalysts. After reduction processes this metal easily forms the alloy with nickel as well as copper does. SEM-EDS measurements confirm the alloy formation on catalysts surface worked in both test reactions. Additionally the formation of appropriate chromates as well as chromites (copper and nickel) was confirmed by TOF-SIMS technique.

Activity tests reveal rather insignificant catalytic effect for binary oxide alone in both reactions. Introduction of copper results in an increase of catalytic activity about ten times (from 10^{-7} to 10^{-6} mol_{CH3OH}). Modification by gold increases catalytic performance insignificantly (about 10%) in MS reaction, whereas for partial methane oxidation the modification by gold has no influence on activity but improves the carbon deposition resistance significantly. After 24 h reaction run for 5%Ni/Cr/Al_3O_6 catalyst was observed 10% of carbon deposit formation and 7% drop of methane conversion but in the case of 5%Ni-2%Au/$CrAl_3O_3$ catalyst the carbon deposit formation was below 1% after 24h reaction run and activity drop was not noticeable.

Significance

1. The formation of chromate (in the case of copper) and chromites (in the case of nickel) was confirmed by TOF-SIMS and XRD techniques
2. Formation of metallic alloys between gold and copper and gold and nickel was observed in reductive conditions, as well as during PM and MS reaction runs.
3. Gold addition has no influence on the TPR profiles in the case of nickel or copper supported catalysts
4. Binary oxide $CrAl_3O_6$ alone exhibits catalytic activity in both POM and MS test reactions, introduction of copper or nickel improves catalytic performance significantly.
5. Modification by gold influences slightly on the activity, but improve the carbon resistance significantly

References

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