



Alkylation of Isopropanol with Ethanol over Heterogeneous Catalysts

Polina A. Zharova^{*a}, Andrey V. Chistyakov^a, Mark V. Tsodikov^a, Sergey A. Nikolaev^b, Michele Corbetta^c, Flavio Manenti^c

^a A.V. Topchuev Institute of Petrochemical Synthesis, Leninskiy prospect, 29, Moscow, 119991, Russian Federation

^b Lomonosov Moscow State University, GSP-1, 1-3 Leninskiye Gory, Moscow, 119991, Russian Federation

^c Politecnico di Milano, Dipartimento di Chimica, Piazza Leonardo da Vinci, 32, 20133 Milano, Italy
zharova@ips.ac.ru

The importance of synthesis of carbon-carbon bonds is reflected by the fact that Nobel Prizes in Chemistry have been given to this area: The Grignard reaction (1912), the Diels-Alder reaction (1950), the Wittig reaction (1979), the olefin metathesis Y. Chauvin, R.H. Grubbs and R.R. Schrock (2005), the palladium-catalyzed cross-coupling reactions to R. F. Heck, A. Suzuki, E. Negishi (2010). For the first time ever alkylation of isopropanol with ethanol was carried out over heterogeneous 0.2-1 wt.% Au and/or 0.02-0.3 wt.% Ni – containing catalysts without any sacrificial agents and/or presence of acidic/base additives. The catalyst containing 0.2 wt.% Au and 0.18 wt.% Ni supported on γ -Al₂O₃ was found to be the most selective in the cross-coupling route. Total selectivity of coupling products reached up to 70 %, conversion of the both initial alcohols was 50 %. Structural investigations of the Au, Ni – containing catalysts permitted to determine probable active sites peculiarities that provide effective one-pot alkylation of isopropanol with ethanol.

1. Introduction

The development of bio-based alternatives for the production of fuels and chemicals has grown significantly in recent years. Ethanol is a well-known renewable resource that annual production is about 110 million tons from which 100 million tons used as fuels and chemicals (Kaltschmitt et al., 2014). Another bio product is isopropanol. Its attractive production based on cellulose fermentation using *E. coli* enzymes are under great consideration nowadays (Soma et al., 2012). One of approaches aimed towards the catalytic valorisation of readily available ethanol and isopropanol into more advanced products is its cross-coupling directed to the pentanol-2 production that is a piperylene precursor. Piperylene is a valuable monomer that is used in manufacture of plastics, adhesives and resins.

Among a known abundance methods of alcohols synthesis, C-C bond formation is a pivotal method to construct intricate molecules from some simple substrates. In spite of the great attention is given by scientific community to this process, it still has some disadvantages in the economic and environmental points of view. Here we report an alternative method one-pot β -alkylation of secondary alcohols with primary alcohols that first time ever was carried out over heterogeneous catalysts.

2. Materials and Methods

Analytical grade ethanol (96 %) was used without further purification. For catalytic experiments, original Au-containing catalysts samples were used. Gamma Al₂O₃ with S=160 m²/g was used as a support for metal nanoparticles. Au/Al₂O₃ catalysts were produced by deposition-precipitation as described by Nikolaev et al. (2013). In typical experiment an aqueous solution of HAuCl₄ was adjusted to pH = 7.0 by adding NaOH (0.1 M), then the support was dispersed in the solution with stirring for 1 h. This precursor was washed to remove Cl⁻, dried in air at 298 K for 24 h and calcined in air at 623 K for 3 h. NiO/Al₂O₃ catalyst was produced by impregnating Al₂O₃ (calcined at 623 K for 3 h) with an aqueous solution of Ni(NO₃)₂, followed by calcination at

623 K for 3 h. NiO/Au catalysts were produced by impregnating Au/Al₂O₃ catalysts with an aqueous solution of Ni(NO₃)₂, followed by calcination at 623 K for 3 h.

The metal content of the catalysts was determined by atomic absorption on a Thermo iCE 3000 AA spectrometer. The relative error of this method was within ± 1 %. Transmission electron microscopy (TEM) and energy-dispersive X-ray (EDX) analysis of catalysts were carried out on a JEOL JEM 2100F/UHR microscope with 0.1-nm resolution and a JED-2300 X-ray spectrometer, respectively. The size of spherical (SPH) and distorted (DIS) particles was calculated as diameter and maximum linear size, respectively. For each catalyst, 300-380 particles were processed to determine the particle size distribution. The mean particle size was determined as the average size of the most frequent particles. The concentration of SPH particles in the catalyst was calculated as $C(\text{SPH}) = n(\text{SPH}) \times N \times 100 \%$, where $n(\text{SPH})$ is the number of SPH particles, N (300-380) is the number of processed particles. The concentration of DIS particles was calculated in the same manner. X-ray diffraction (XRD) analysis was carried out on a Rigaku D/MAX 2500 instrument using Cu K α radiation with a step size of 0.02 ° two-theta (2θ) ranging from 35–70 °. The average size of the gold particles was determined from XRD patterns using the Debye–Scherer formula. The strongest reflection observed with $d = 0.235$ nm was chosen as an analytical reflection for Au(111).

The alkylation of alcohols was performed in a 45 mL high pressure Parr autoclave equipped with magnetic stirring under argon. The reactor was heated up to 275 °C with a heating rate of 20 °C/min. Qualitative and quantitative analyses of the C₁–C₅ hydrocarbon gases were performed by gas chromatography (GC) with a Kristall-4000M chromatograph (detector: FID, carrier gas: He, column: HP-PLOT/Al₂O₃, 50 m \times 0.32 mm). GC analyses of CO, CO₂ and H₂ were performed with a Kristall-4000 chromatograph (detector: TCD, carrier gas: Ar, column: SKT, 1.5 m \times 4 mm). The qualitative composition of the liquid products were identified by gas-liquid chromatography coupled to a mass spectrometry (GLC-MS) using a MSD 6973 - and an Autowt.-150 spectrometer - (EI = 70 eV, catalyst volume = 1 μ l, columns: HP-5MS, 50 m \times 0.32 mm and CPSil-5, 25 m \times 0.15 mm). The quantitative content of the organic compounds was determined by GLC using a Varian 3600 chromatograph (detector: FID, carrier gas: He, column: Chromtec SE-30, 25 m \times 0.25 mm). Calibration of the GLC was carried out with commercial standards using method Haruta et al. (1987).

3. Results and Discussion

Found that over monometallic Au/Al₂O₃ and bimetallic Au-Ni/Al₂O₃ catalysts ethanol and isopropanol converts mainly into pentanol-2 and heptanol-4 (Table 1). Monometallic Ni/Al₂O₃ catalyst is not active in the process at all. Detailed analysis of the reaction products (Table 1) permits to consider that cross-coupling process proceeds according to Scheme 1. On the first step substrates molecules undergo dehydrogenation with acetic aldehyde and acetone formation. Should be noticed that among products we observed a small amount of acetic aldehyde that means aldehyde is more active molecule than acetone is under process conditions. The main by-reaction of aldehyde is self-aldonization resulting in butanol-1, hexanol-1 and octanol-1 formation.

The catalyst containing 0.2 wt.% Au and 0.18 wt.% Ni was found to be the most active one in cross-coupling process. Over this catalyst total selectivity of cross-coupling products reached up to 70.2 % with ethanol and isopropanol conversions about 50 %. The decrease of Ni content leads to substrates conversion decreasing down to 29.3 % for ethanol and 27.7 % for isopropanol and selectivity lowering down to 61,8 %. Also Ni content decreasing leads to deceleration of intermediates hydrogenation that results in increasing of ketones formation selectivity.

The increasing of both Au and Ni concentration in the catalyst up to 1 wt.% and 0.3 wt.%, consequently, leads to initial alcohols conversion increasing but aim products of cross-coupling selectivity lowering. Also the inhibition of hydrogenation of intermediate ketones (pentanone-2, heptanone-4) was observed. Acetone and diethyl ether are the main by-products, that selectivity were 14.2 and 16.1 %, consequently.

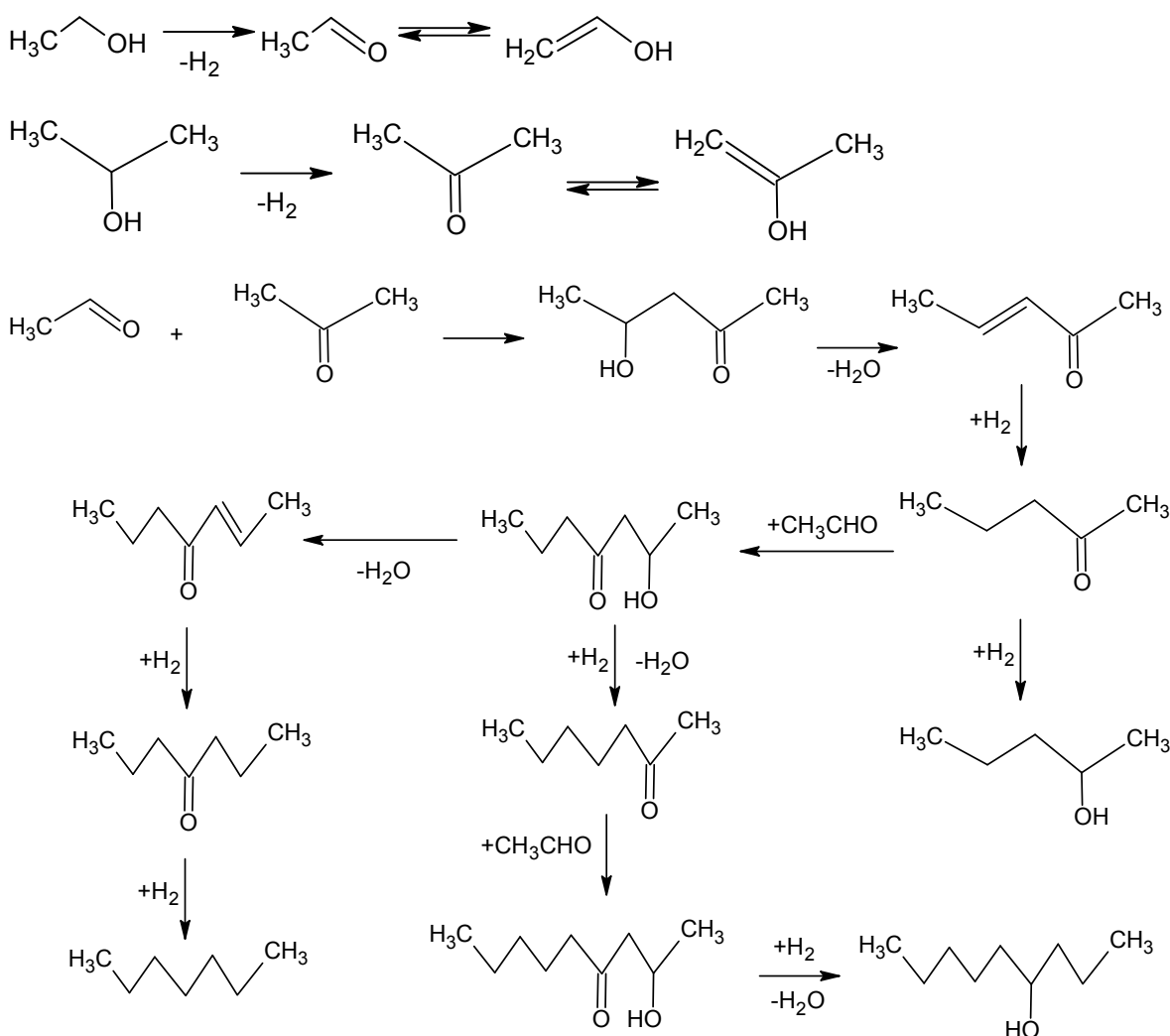
Monometallic catalysts containing 0.2-1 wt.% Au have lower selectivity of coupling products formation than bimetallic catalysts. Should be noticed that size effect of Au particles were observed during ethanol and isopropanol conversion. The decreasing of Au concentration leads to selectivity lowering of alkylation products but conversions of ethanol and isopropanol were increasing. So the smallest Au particles have the highest activity and lowest selectivity. The main by-products over 0.2 wt.% Au/Al₂O₃ catalyst are diethyl ether and acetone. Also one can see that the ratio between aimed alcohols (pentanol-2, heptanol-4) and ketones (pentanone-2 and heptanone-4) significantly lower than one over the most prospective catalyst 0.2 wt.% Au-0.18 wt.% Ni/Al₂O₃. That phenomenon means inhibition of hydrogenation processes.

The diffraction patterns of Ni, Au and Au-Ni catalysts are shown in Fig.1. The diffraction pattern of monometallic Ni/Al₂O₃ catalysts present reflexes at $2\theta = 32.5, 37.6, 39.5, 46.0, 61.1, 66.8$ °, that indicates to the reflection from the faces (220), (311), (222), (400), (511), (440) of alumina (Nikolaev et al., 2013).

Absence of reflections from Ni-containing phase indicates a high dispersion of active component on the support surface. In the diffraction pattern of Au/Al₂O₃ addition of Al₂O₃ present reflexes at 2θ = 38.1, 44.4 and 64.6 °, which are the reflection of the faces (111), (200) and (222) of gold (Nikolaev et al., 2012).

In comparison with Au/Al₂O₃ diffraction peaks of gold in Au-Ni/Al₂O₃ samples broadened, indicating a high dispersion of Au-containing phase. The lack of new reflexes or reflexes shifts in the diffraction patterns from gold in Au-Ni samples, allowing with high probability to eliminate the formation of alloys with unlimited solubility or intermetallic compounds with a regular structure.

Scheme 1.



Electronic state of metal in the Au-Ni, Au and Ni catalysts was studied previously by X-ray photoelectron spectroscopy, and the results are shown by Tkachenko et al. (2008). Found that Ni is presented in the oxide form on the surface of Ni/Al₂O₃. Gold is presented as metal in the Au/Al₂O₃ sample. Compared with the catalyst Au/Al₂O₃ binding energy of Au 4f_{7/2} electrons according to XPS spectrum of Au-Ni/Al₂O₃ catalyst shifted by + 0.3 eV. This result points to the fact that in addition to the zero-valent gold in the Au-Ni/Al₂O₃ formed cations Au (+ n), 0 < n < 1. The content of Au (+ n) is low and of the order of 10-20 at.%. Apparently, in the Au-Ni catalyst phase contacts Au (0) and NiO leads to electron transfer from gold to nickel oxide. As a result, the oxygen of the nickel oxide lattice interact with gold forming AuO_y oxide.

On the Au/Al₂O₃ catalyst surface areas exist ordering of the atoms belonging to gold particles with an average size of 10 ± 2 nm (Fig. 2) according to TEM and EDX analysis data. Formation in Au/Al₂O₃ of relatively large gold particles caused by weak metal-support interaction, which leads to sintering of noble metal particles at the stage of calcination the catalyst with impregnated precursor. In comparison with Au/Al₂O₃ average particle size in the Au-Ni/Al₂O₃ is shifted towards smaller particles possesses average size about 5 nm (Fig. 3). The shift of the average particle size in the Au-Ni/Al₂O₃ indicates that nickel oxides stabilize small particles of gold

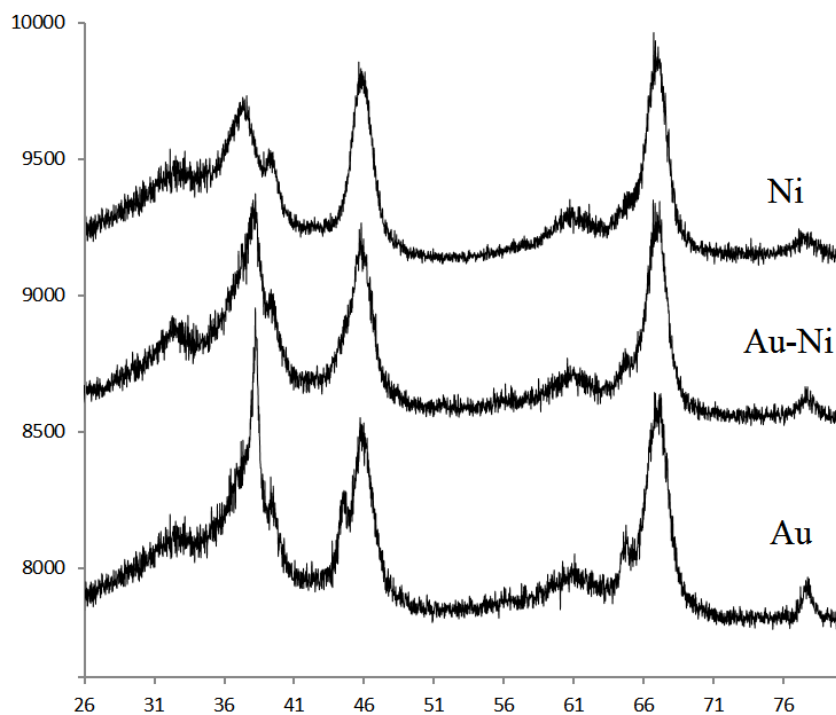


Fig. 1. XRD data for Ni/Al₂O₃, Au-Ni/Al₂O₃ and Au/Al₂O₃ catalysts

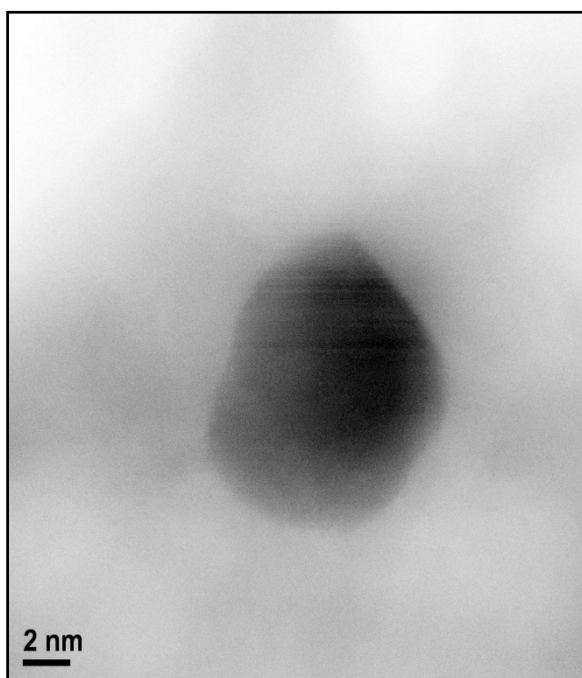


Fig. 2 . TEM images of the supported nanoparticles in the catalyst Au/Al₂O₃

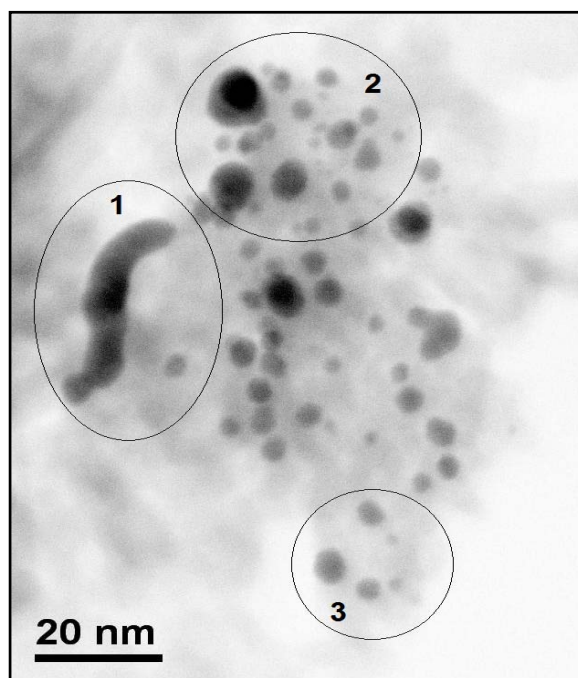


Fig.3 TEM images of the supported nanoparticles in the catalyst Au-Ni/Al₂O₃

4. Conclusions

In conclusion, we report that Au-Ni systems effectively catalyze one-pot alkylation of isopropanol with ethanol resulted in pentanol-2 and heptanol-4 formation. The catalyst containing 0.2 wt.% Au and 0.18 wt.% Ni supported on γ -Al₂O₃ was found to be the most selective in the cross-coupling route. Total selectivity of

coupling products reached up to 70 %. conversion of the both initial alcohols was 50 %. Structural investigations of the Au, Ni – containing catalysts permitted to determine two main factors effected on catalytic activity: structural and charge effects. In the case of bimetallic catalysts clusters of $Au^{\delta+}_n-Ni^{+2}_n-Au^{\delta+}_n-Ni^{+2}_n$ are formed that provide effective coordination of substrates with active surface and make catalytic cycle via the most suitable charge state of gold.

Acknowledgments

This work was financially supported by Russian Scientific Foundation Grant № 15-13-30034 and used the equipment of M.V. Lomonosov Moscow State University (Program of MSU Development).

Reference

- Haruta M., Kobayashi T., Sano H., Yamada N., 1987. Chem. Lett., 16, 405–408.
- Kaltschmitt M., Hofbauer H., 2014. Biomass Conversion and Biorefinery. Springer-Verlag, Berlin Heidelberg. DOI 10.1007/s13399-014-0155-1
- Nikolaev S.A., Chistyakov A.V., Chudakova M.V., Kriventsov V.V., Yakimchuk E.P., Tsodikov M.V.//J. Catal. 2013. V. 297. P. 296–305.
- Nikolaev S.A., Pichugina D.A., Mukhamedzyanova D.F. 2012. Gold Bulletin., V.45. №4. P.221
- Soma Y., Inokuma K., Tanaka T., Ogino Ch., Kondo A., Okamoto M., and Hanai T., 2012. Journal of Bioscience and Bioengineering. VOL. 114 No. 1. 80-85
- Nikolaev S.A., Zhanaveskin L.N., Smirnov V.V., Averianov V.A., Zhanaveskin K.L., 2009. Uspekhi khimii. T.78. №3. C.248.
- Tkachenko O.P., Kustov L.M., Nikolaev S.A., Smirnov V.V., Klementiev K.V., Naumkin A.V., Volkov I.O., Vasil'kov A.Yu., Murzin D.Yu., 2009. Topics in Catalysis., V.52. №4. P.344.
- Zharova P.A., Chistyakov A.V., Tsodikov M.V., Corbetta M., Manenti F., 2015. Cross-Coupling of Bio-oxygenates over Heterogeneous Catalysts. Chemical Engineering Transaction. 43. p.415-420.