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Alkylation of Isopropanol with Ethanol over Heterogeneous Catalysts

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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 Witting 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-Al_2O_3 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 Al_2O_3 with S=160 m^2/g was used as a support for metal nanoparticles. Au/Al_2O_3 catalysts were produced by deposition-precipitation as described by Nikolaev et al. (2013). In typical experiment an aqueous solution of $HAuCl_4$ 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/Al_2O_3 catalyst was produced by impregnating Al_2O_3 (calcined at 623 K for 3 h) with an aqueous solution of $Ni(NO_3)_2$, followed by calcination at

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623 K for 3 h. NiO/Au catalysts were produced by impregnating Au/Al_2O_3 catalysts with an aqueous solution of $Ni(NO_3)_2$, 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(SPH) = n (SPH) × N × 100 %, where n(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 Kα 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 C_1–C_5 hydrocarbon gases were performed by gas chromatography (GC) with a Kristall-4000M chromatograph (detector: FID, carrier gas: He, column: HP-PLOT/Al_2O_3, 50 m × 0.32 mm). GC analyses of CO, CO_2 and H_2 were performed with a Kristall-4000 chromatograph (detector: TCD, carrier gas: Ar, column: SKT, 1.5 m × 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 μl, columns: HP-5MS, 50 m × 0.32 mm and CPSil-5, 25 m × 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 × 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/Al_2O_3 and bimetallic Au-Ni/Al_2O_3 catalysts ethanol and isopropanol converts mainly into pentanol-2 and heptanol-4 (Table 1). Monometallic Ni/Al_2O_3 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.

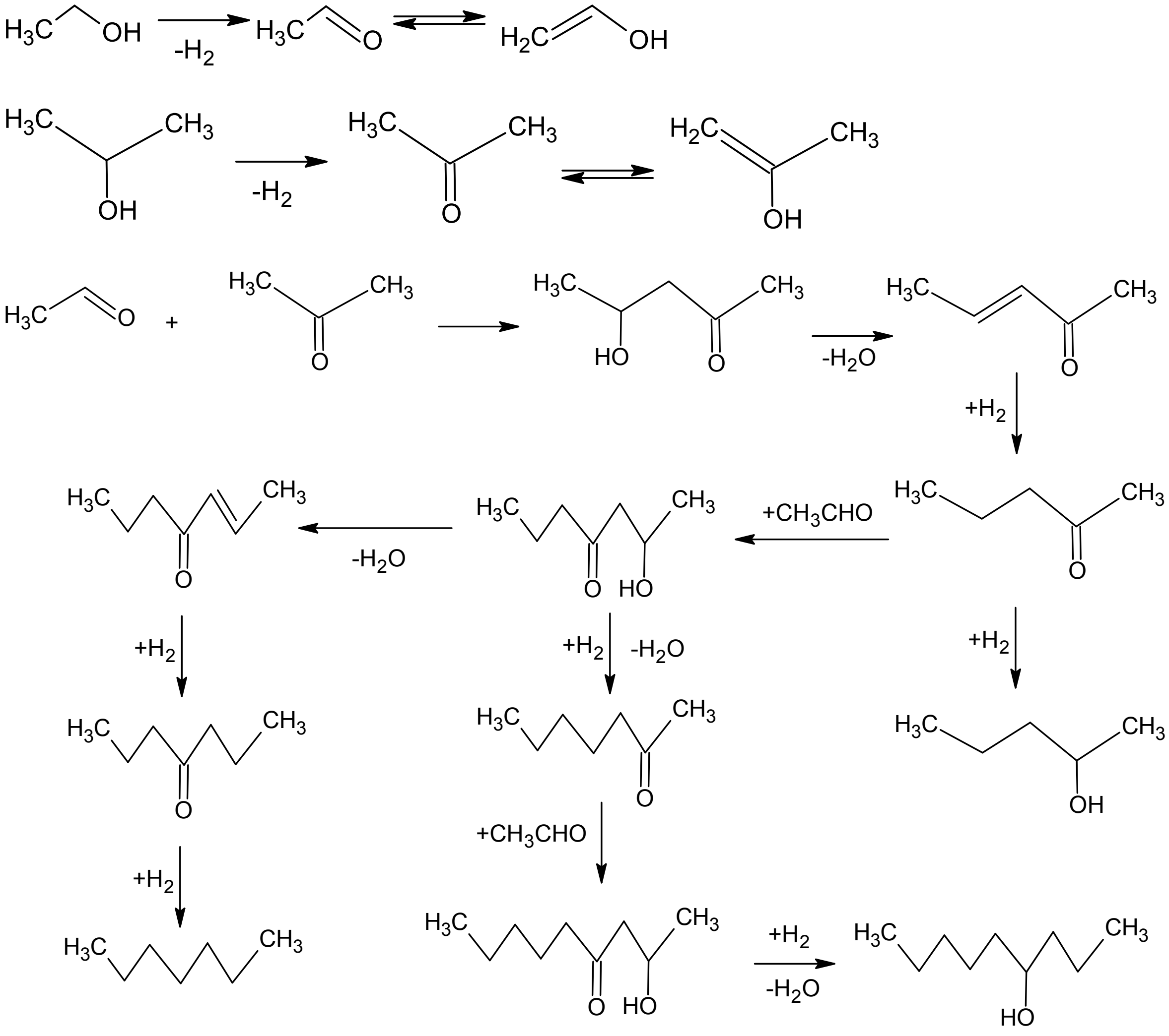
Monometallic catalysts containing 0.2-1 wt.% Au have lower selectivity of coupling products formation than bimetallic catalysts. Should be noticed that size effect of Au particles were observed during ethanol and isopropanol conversion. The decreasing of Au concentration leads to selectivity lowering 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/Al_2O_3 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 hepnanone-4) significantly lower than one over the most prospective catalyst 0.2 wt.%Au-0.18 wt.% Ni/Al_2O_3. 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/Al_2O_3 catalysts present reflexes at 2θ = 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/Al_2O_3 addition of Al_2O_3 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/Al_2O_3 diffraction peaks of gold in $Au\text{-}Ni/Al_2O_3$ 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 4f7/2 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 AuOy oxide.

On the Au/Al_2O_3 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/Al_2O_3 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/Al_2O_3 average particle size in the $Au\text{-}Ni/Al_2O_3$ is shifted towards smaller particles possesses average size about 5 nm (Fig. 3). The shift of the average particle size in the $Au\text{-}Ni/Al_2O_3$ indicates that nickel oxides stabilize small particles of gold on the support surface. With the TEM-EDX data found that 20% of the particles in the Au-Ni/Al_2O_3 comprised of non-interacting particles of Au and Ni oxide particles, while the remaining 80% is the composition of the bimetallic contact between a nickel oxide particles and small clusters of gold.

Some contribution to the high activity of bimetallic Au-Ni/Al_2O_3 catalyst can give the formation of new centers of gold cations Au (+n). 0<n<1. Consider this idea in more detail. From Scheme 1 one can see that the growth of the alcohols hydrocarbon skeleton (for example pentanol-2) passes through the dehydrogenation-hydrogenation steps. It is known that these processes are accompanied by changes of catalytic metal oxidation ratio from M(n) to M(n+2) (Nikolaev et al.. 2009). For the Au/Al2O3 catalyst changes in oxidation state of gold may be presented as next cycle Au (0) → Au (+2) → Au (0). which includes uncharacteristic for gold oxidation state (+2). Therefore. the hydrogenation-dehydrogenation of hydrocarbons over zero-valent Au clusters in the Au/Al_2O_3 take place at relatively low speed. In the case where. on the surface of gold clusters are formed by individual atoms in oxidation state close to (+1) rapid cycle becomes possible consisting of characteristic gold oxidation states Au (+1) → Au (+3) → Au (+1) . Therefore. the processes of hydrocarbons dehydrogenation-hydrogenation (and thus the formation of high molecular alcohols of Scheme 1) on cations in Au Au-Ni/Al2O3 should proceed at a higher speed.

Heigh selectivity of alkylation products over Au-Ni/Al_2O_3 catalyst in comparison with monometallic analogue Au/Al2O3 can be explained by changes in the morphology of the active cites of the catalyst. Fig. 3 shows that in the case of bimetallic catalysts clusters of Au_n-Ni_n-Au_n-Ni_n are formed. Obviously. such close deposition of metals clusters favour multiple molecules coordination of ethanol and isopropanol and facilitated growth of advanced hydrocarbon skeleton structures (Scheme 1).

Table 1. Products formation selectivity and conversions of ethanol and isopropanol (275 °C, 150 atm, 5 h on stream).

catalyst	0,2Au-0,02Ni	0,2Au-0,06Ni	0,2Au-0,18Ni	1Au-0,3Ni	1Au	0,5Au	0,2Au
total selectivity of alkylation product, %	61.8	66.9	70.2	53.6	49.2	41.5	33.8
ethanol conversion. %	29.3	38.2	49.9	58.7	20.8	26.2	46.7
isopropanol conversion. %	27.7	36.7	50.7	61.8	23.5	33.8	56.4
product	selectivity. %						
propane	3.7	2.3	2.3	1.3	2.6	2.4	4.3
acetic aldehyde	0.2	0.2	0.1	0.3	3.1	3.6	2.9
acetone	9.1	10.6	7.4	14.2	12.2	22.7	16.6
ethyl isopropyl ether	2.4	2.8	1.0	4.7	4.4	4.4	6.9
diethyl ether	6.2	4.1	3.5	16.1	18.8	11.8	26.2
ethylacetate	0.3	0.5	0.2	0.6	0.8	2	0.8
butanol-1	15.0	10.2	13.2	7.7	7.9	8.1	8.0
pentanone-2	14.2	15.1	13.5	14.2	18.8	14.3	10.4
pentanol-2	34.7	37.2	40.5	25.6	19.6	19.1	19.1
hexanol-1	0.4	0.7	0.4	0.6	0.3	1.7	0.2
butylacetate	0.1	0.9	0.8	0.2	0.2	1.5	0.1
heptanone-4	3.1	3.4	2.5	5.2	4.8	3.2	1.1
heptanone-2	1.1	1.9	2.1	1.5	0.3	0.2	0.1
heptanol-4	7.0	7.2	9.8	6.3	4.8	4.0	2.8
heptanol-2	0.8	0.9	0.7	0.4	0.2	0.3	0.1
octanol-1	0.8	0.9	0.9	0.8	0.4	0.2	0.3
nonanone-4	0.4	0.5	0.6	0.3	0.1	0.1	0.1
nonanol-4	0.5	0.7	0.6	0.2	0.5	0.3	0.1
Σ	100	100	100	100	100	100	100

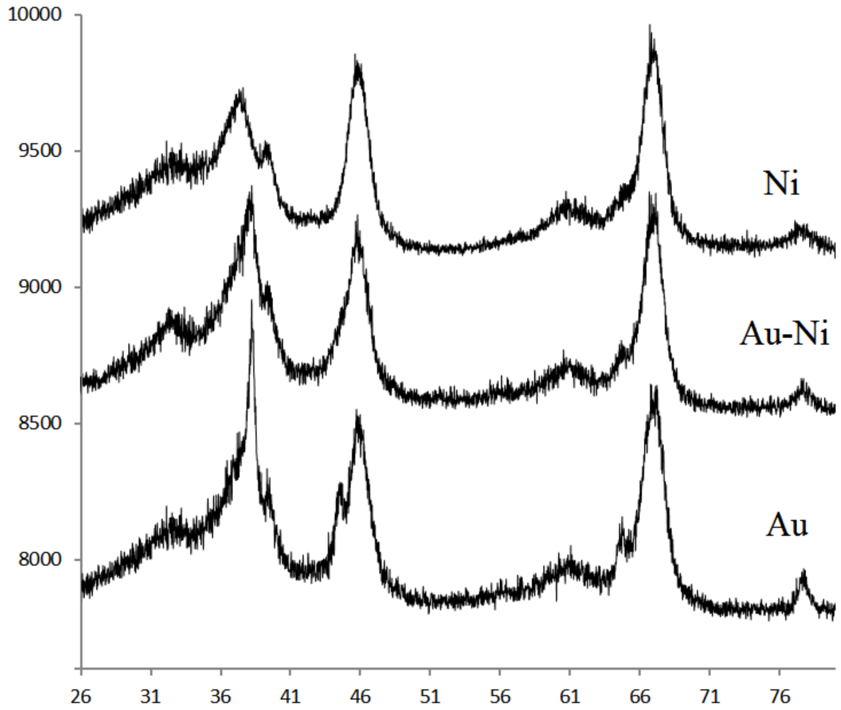


Fig. 1. XRD data for Ni/Al_2O_3. $Au\text{-}Ni/Al_2O_3$ and Au/Al_2O_3 catalysts

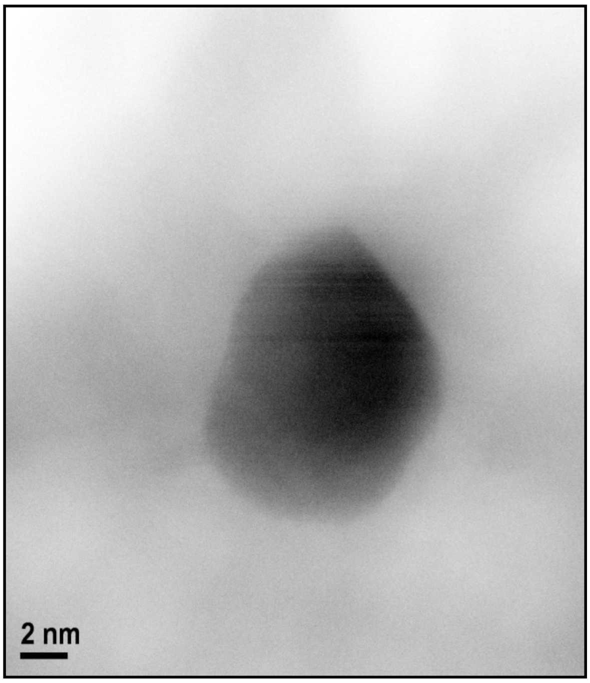


Fig. 2 . TEM images of the supported nanoparticles in the catalyst Au/Al_2O_3

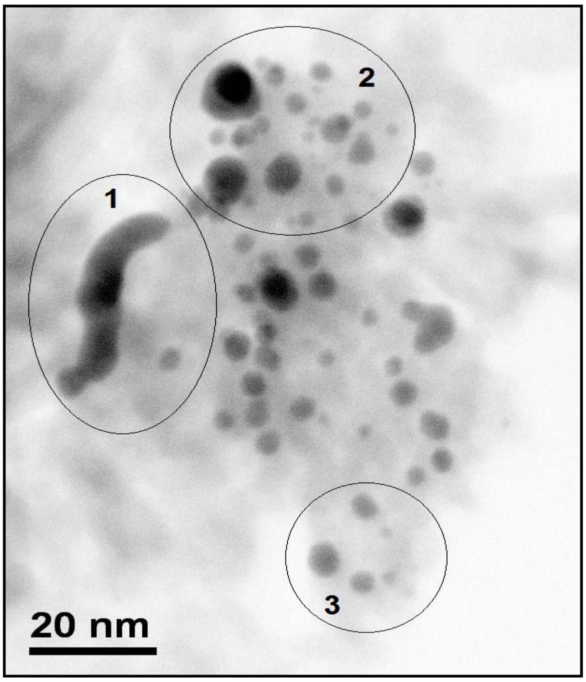


Fig.3 TEM images of the supported nanoparticles in the catalyst $Au\text{-}Ni/Al_2O_3$

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 $\gamma\text{-}Al_2O_3$ 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.

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