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Mixed Cu-Ni-Co nano-metal oxides: A new class of catalysts for styrene oxidation

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Abstract

A series of mixed nano-metal oxides of Cu-Ni-Co on γ -alumina with different metal loadings have been synthesized through the ultrasonic cavitation-impregnation method. All the prepared catalysts were analyzed by BET, ICP, XRD, SEM-EDS and TEM. The heterogeneous catalytic oxidation of styrene was investigated using *tert*-butyl hydroperoxide (TBHP) as an oxidizing agent and acetonitrile as a solvent under mild conditions. The influence of the metal loadings, reaction temperatures, oxidizing agents and styrene/oxidant molar ratio was investigated on the styrene conversion and on the selectivity to benzaldehyde and styrene oxide. Key words: Mixed metal oxides, Oxidation, Styrene conversion, C=C cleavage, Benzaldehyde

1. Introduction

Due to increasing demand for clean technologies in chemical process engineering, much attention has recently been paid to catalytic processes, which include removal of toxic and expensive reagents, minimization of by-products, and simplification of workup procedures [1]. Olefin oxidation is an important transformation in the production of fine and pharmaceutical grade chemicals. Metal-catalyzed oxidation of olefins can give rise to a whole variety of organic products [2,3], e.g. aldehydes, ketones, alcohols, epoxides, and acids.

Styrene oxidation at the side chain is of considerable interest. Traditionally, many waste byproducts are produced during the reaction over homogeneous catalysts [4]. This reaction has been studied using *tert*-butyl hydroperoxide (TBHP) over supported gold nanocatalysts in benzene at reflux [5]. Solvent free oxidation of styrene over undecamolybdophospate supported on neutral alumina has been reported recently [6], as has the oxidation of styrene to benzaldehyde by anhydrous hydrogen peroxide on γ -alumina-supported V₂O₅ nanoparticle catalysts [7]. Simple transition metal oxides, like NiO, CoO and MoO₃ are known for the selective oxidation of styrene by TBHP and among these NiO showed the best performance [8]. Most systems tend to give styrene oxide [9-11], although, dendrimer derived titania-supported Au catalysts show 41% styrene conversion with TBHP in cyclohexane to give benzaldehyde as major product [12].

Benzaldehyde is a very valuable chemical that has widespread application in perfumery, pharmaceuticals, dyestuffs, and agro chemicals. It is the second most important aromatic molecule (after vanillin) used in the cosmetics and flavor industries [6]. Styrene oxide can be

used for producing epoxy resin diluting agents, ultraviolet absorbents, flavoring agents, etc., and is also an important intermediate for organic synthesis, pharmacochemistry and perfumery.

Being a terminal olefin, styrene is difficult to oxidize. Despite many efforts to increase the conversion and selectivity to desired products, only few catalytic systems with multi transition metal oxides have been developed. Many reports exist on mesoporous materials as catalyst supports with high surface areas and defined pore-sizes [13-19] and these, with transition metal oxides, might enhance catalytic activity in styrene oxidation. It seemed likely that the use of nano-phased and well dispersed catalysts would benefit the catalytic activity due to the increase in catalyst surface area and physical-chemical interactions. Thus, by mixing the nanometal oxides into alumina using ultrasonic cavitation-impregnation, we aimed at achieving good metal dispersion. We now report in this study a new class of inexpensive mixed nano-metal oxides of 5-30 wt% loadings of Cu-Ni-Co on γ -Al₂O₃, as highly active and selective heterogeneous catalysts for styrene oxidation using TBHP as co-oxidant with high selectivity to benzaldehyde.

2. Experimental details

2.1. Catalyst preparation

The ultrasonic cavitation-impregnation method was used. Appropriate amounts of the metal precursors, $Cu(NO_3)_2 \cdot 3H_2O$ (Sigma-Aldrich), $Ni(NO_3)_2 \cdot 6H_2O$ (Sigma-Aldrich) and $Co(NO_3)_2 \cdot 6H_2O$ (ACE) were dissolved in distilled water and added to γ -Al₂O₃ (Alfa-Aesar).

To get uniform dispersion, magnetic stirring of 300 rpm and ultrasonic cavitation at 43 KHz frequency (MRC Ultrasonic System, D150H) was applied at room temperature. The excess water of the slurry was evaporated at 70°C under continuous stirring. The catalysts were dried at 110°C for 16 h, then calcined at 550°C for 5 h, to give the 5, 10, 20 and 30 wt% ternary metallic nanocatalysts. The catalysts compositions are given in **Table 1**. The codes 5CuNiCoA, 10CuNiCoA, 20CuNiCoA, 30CuNiCoA, mean 5, 10, 20, 30 wt% total transition metal oxides on the γ -Alumina (A) support. The intermetallic ratio of copper oxide, nickel oxide and cobalt oxide was kept constant in the range.

2.2. Characterizations techniques

The Brunauer-Emmett-Teller (BET) surface area and porosity was determined using a Micromeritics Tristar II instrument. The metal loading was determined by a Perkin Elmer Inductive coupled plasma Optical Emission Spectrometer Optima 5300 DV. The metal dispersion and crystallite size were determined by CO chemisorption using a Micromeritics ASAP 2020. All catalysts were viewed under a Zeiss 'Ultra plus' SEM and a Jeol JEM-1010 Electron Microscope (TEM). Powder XRD was performed on a Bruker D8 Advance instrument.

2.3. Catalyst testing

The oxidation of styrene was usually carried out at 40° C (reaction mixture temperature) using catalyst (5 mg) and styrene (96 mmol) in CH₃CN (2.5 ml) for 24 h in a two-neck flask equipped with a condenser in an oil bath with stirring. The molar ratio of styrene to TBHP (70% in water) was kept at 1:1.5. The reactant and products of the reaction were analyzed by gas chromatography (Perkin Elmer Autosystem). Only products with a benzene ring were considered in the calculation of selectivity.

3. Results and discussion

3.1. Characterization

The surface areas and pore volumes of the ternary catalysts decreased from 5 wt% to 30 wt% total metal loadings of copper, nickel and cobalt on γ -Al₂O₃ (**Table 1**). The support surface was completely covered due to the higher metallic loading in 30CuNiCoA, giving the lowest surface area. **Fig. 1a** shows the nitrogen adsorption-desorption isotherms of the ternary catalysts calcined at 550°C for 5 h. The isotherms show IUPAC type IV patterns with sharp inflections of nitrogen adsorbed volume at P/P₀ of about 0.65 (type H2 hysteresis loop), indicating the existence of mesopores and these play a significant role in catalyst activity in the presence of metal oxides. All the prepared materials have mesopores with narrow pore size distribution (**Fig. 1b**). BET results revealed that the texture of the catalysts was strongly dependent on the total metal loadings, resulting in significant changes of the surface areas as well as the total pore volumes. Major changes in textural properties were observed in 10, 20 and 30 wt% catalyst samples. ICP results obtained were in the expected range (**Table 1**).

The powder XRD patterns (**Fig. S1**) of the prepared ternary oxides on alumina support show the different metal oxides phases of CuO (JCPDS card no. 5-066), NiO (JCPDS 4-00835), Co_3O_4 (JCPDS 42-1467) and γ -Al₂O₃ (JCPDS 10-425). The increase in the metal loadings resulted in a slight increase in the 2 θ values in the XRD diffractograms. Some overlapping of diffraction peaks was found among the various metal oxides in all the samples and similar patterns were observed for all ternary catalysts. Because of the low metal loadings in the case of 5CuNiCoA and 10CuNiCoA, no peaks of metal oxides were seen, due to the detection limit of XRD. The CO chemisorption study of the ternary catalysts revealed a decrease in the average crystallite size of all metals from higher metal loadings to lower metal loadings (**Table 2**) and further information is given in the supplementary data.

The morphologies of the ternary Cu-Ni-Co oxide catalyst particles on the γ -Al₂O₃ surface are visible in the higher magnification SEM images (**Fig. 2a-c**) and their dispersion on alumina was also confirmed by EDS mapping, shown for 10CuNiCoA (**Fig. 3**). This revealed that all metal particles are well distributed throughout the surface of the support. As the metal loadings increases from 10 to 30 wt%, the size of the catalyst particles also increases to an extent due to agglomeration of the small metal oxide nanoparticles. In the case of low metal loaded samples, 5CuNiCoA and 10CuNiCoA show good individual particle dispersion and very little agglomeration is observed. The TEM images (**Fig. 2d-f**) of all the catalyst powders show the effect of metal loadings on the size of catalyst particles and their dispersion on the support. On higher magnification, the metal oxide particles appear very clear. All images show round shaped metal oxide particles, as well as elongated rod/needle-like alumina particles. The size of these mixed metal oxide particles is in the range of 10-30 nm and more agglomeration is seen in the case of 30CuNiCoA.

3.2. Catalyst evaluation

3.2.1. Optimization

The catalysts were tested in the oxidation of styrene. Effects of solvent, oxidant, catalyst amount, reaction temperature, reaction time and the styrene/oxidant molar ratio were optimized using 10CuNiCoA as catalyst.

The effect of the amount of catalyst on the oxidation reaction was explored by using 5% (5 mg), 10% (10 mg), 15% (15 mg) of 10CuNiCoA, by weight of styrene, keeping all other parameters fixed. The conversion and selectivity were not affected by the amount of catalyst, due to the good metal dispersion on the high surface area support. Therefore, 5 mg catalyst was taken for all further studies.

Initially, the reaction was carried out using dichloromethane and acetonitrile, which are used commonly in these types of reactions. The best performance of the catalyst was found in acetonitrile, as it fully dissolves both styrene and TBHP and thus facilitates the oxidation reactions.

Two different oxidizing agents were initially employed, namely H_2O_2 and TBHP, at 40°C. The oxidation reaction with hydrogen peroxide gives 42 % conversion after 24 hour but very poor selectivity towards benzaldehyde and styrene oxide. It forms a whole variety of oxidized products like benzaldehyde, styrene oxide, acetophenone, phenyl acetaldehyde and 1-phenyl-ethane-1,2-diol. However, with TBHP, best conversion (73%) and good selectivity towards benzaldehyde (72%) and styrene oxide (19%) was obtained after 24 hours for 10CuNiCoA.

The effect of styrene/oxidant molar ratio was also examined to get maximum conversion and selectivity towards benzaldehyde and styrene oxide. After 24 h at 40°C, the 1.0:0.5, 1.0:1.0, and 1.0:1.5 molar ratios gave 46%, 60%, and 73% styrene conversion, respectively, but no influence on the selectivity to desired products was observed. A molar ratio of 1.0:1.5 styrene/oxidant was thus chosen for further studies.

The effect of temperature was investigated at room temperature, 40 and 55°C, on the oxidation of styrene using acetonitrile as a solvent with 5 mg catalyst and a styrene to TBHP ratio of 1.0:1.5. At RT, 40 and 55°C, the styrene conversion was found to be 22%, 53% and 81%, respectively, after 9 h of reaction (**Fig. 4**). At 40°C, selectivity to benzaldehyde was 50% and 7% was to styrene oxide and at 55°C, conversion was good but selectivity to benzaldehyde was 39% with 16% to styrene oxide. At 55°C, because of the higher temperature, the reaction followed both reaction pathways shown in **Scheme 1** simultaneously and hence a decrease in benzaldehyde selectivity was observed. So, a 40°C reaction temperature is the preferred temperature for the oxidation of styrene over these catalysts.

The ideal conditions for maximum conversion of styrene to benzaldehyde and styrene oxide are thus a mole ratio of styrene to TBHP of 1.0:1.5, 40°C, with 5 mg catalyst, in acetonitrile.

3.2.2. Role of ternary catalysts for styrene oxidation

The utility of this new class of ternary metal oxide catalysts for styrene oxidation was further explored under the above mentioned, optimized reaction conditions. Since the Cu-Ni-Co oxides are on an alumina support, the behavior of the support (without transition metal oxide) was investigated under similar reaction conditions and it showed only 4% styrene conversion. Hence, the conversion exhibited with the catalysts is clearly dependent on the nature of the mixed metal oxides and not the alumina itself.

As the metal loading increased from 5 to 30 wt%, the conversion of styrene also increased (Fig. 5). This can be due to the increased availability of the ternary metal oxide active sites, providing more active centres for reaction. The benzaldehyde selectivity decreases from 72 to 58% with increasing total metal loadings at the end of the 24 h reaction period. The selectivity of styrene oxide and 1-phenylethane-1,2-diol was found in the range of 18-19% and 8-9%, respectively, in all reactions after 24 h. Other products, i.e. acetophenone and phenyl acetaldehyde, total selectivity was found to be 11% and 14% in the case of 20CuNiCoA and 30CuNiCoA catalysts respectively, but the 10CuNiCoA catalyst showed only 1% total selectivity to these two products. For all the catalysts, turnover frequencies (TOF), defined as mmols of styrene converted per gram of catalyst per hour, range between 5 to 7, comparable to other systems [8], and the carbon balance of all reactions is between 91 to 93%, the balance being CO_2 (Table S1). To identify the role of single metal catalysts, a series of monometallic catalyst with 6 wt% copper, 3 wt% nickel and 1 wt% cobalt supported on alumina were prepared by the same method and tested under similar reaction conditions. Results show 42%, 24% and 25% styrene conversion, respectively, with selectivities of benzaldehyde in the range of 30-50%, styrene oxide in the range of 11-20% and other products in the range of 6-35%.

Overall best catalytic activity and benzaldehyde selectivity was found for 10CuNiCoA. An appropriate metal loading, as well as uniform metal dispersion, tends to facilitate specific product selectivity. Optimum metal loadings may affect the surface properties and number of reactive sites. Activity increases due to the increased number of active sites. The addition of the

copper decreased the crystal sizes of both Ni and Co and increased the metal dispersion, as measured by CO chemisorption (**Table 2**). In addition to the smaller particle sizes, the increased metal dispersion could contribute towards the better activity of the catalysts. The homogenous dispersion of small sized metal particles not only increases the activity by exposing a large number of active sites, but also the possible oxygen transfer to the support.

In general, oxides of Ni and Cu show greater Brønsted acidity than Co oxide [20]. Due to the high Lewis basic nature of the cobalt, the catalyst contains an even distribution of Lewis basic sites and Brønsted acidic sites. The oxidant adsorbs on the surface of the catalyst due to its Brønsted acidic nature and the oxygen from the oxidant desorbs to the support due to the Lewis acidic nature. Thus, this catalytic reaction follows a probable pathway similar to the Eley-Rideal mechanism [21]. The reactive sites would favor the formation of benzaldehyde as a major product in agreement with the experimental results.

It is known that the styrene oxidation at the side chain can lead to various reaction products, depending on the catalyst and reaction conditions. Two major reactions take place. They are the oxidative C=C cleavage into benzaldehyde and epoxidation [6]. However, under the present catalysis conditions, the major oxidation product obtained was benzaldehyde. This may be due to (i) direct oxidative cleavage of C=C of styrene and (ii) fast conversion of styrene oxide to benzaldehyde.

Under the optimized reaction conditions, the control experiment with styrene oxide as a substrate was carried out to confirm the reaction pathway (**Scheme 1**). The results indicate that styrene oxide converts into acetophenone and phenyl acetaldehyde. This proves that benzaldehyde formed through only the direct oxidative cleavage of the C=C bond of styrene, but not through the fast conversion of styrene oxide to benzaldehyde. These catalysts thus have the special property of stimulating direct oxidative cleavage of C=C so that benzaldehyde is the major product.

4. Conclusion

In summary, novel heterogeneous mixed Cu-Ni-Co nano-metal oxide catalysts have been successfully synthesized, characterized and proven highly successful for the oxidation of styrene with TBHP as an oxidant under mild reaction conditions. All ternary catalysts showed good

oxidative activity even at low temperature, due to good dispersion and a cooperative effect produced by the mixed metals on the high surface area mesoporous support.

The main products of the styrene oxidation reaction were benzaldehyde and styrene oxide. The conversion and selectivity towards benzaldehyde was highest i.e. 73% and 72%, respectively, with minimal byproducts formed in the case of 10CuNiCoA. The superiority of this inexpensive catalyst is likely due to synergistic interaction between the metals coupled with high dispersion.

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Captions

Table captions:

- Table 1 Surface area and metal composition of the catalysts
- Table 2 Metal dispersion of γ-Alumina supported ternary catalysts

Figure captions:

- Fig. 1 (a) N₂ Adsorption-desorption isotherms and (b) pore size distribution of ternary catalysts
- Fig. 2 (a,b,c) SEM and (d,e,f) TEM images of the 10CuNiCoA, 20CuNiCoA, 30CuNiCoA catalysts respectively
- Fig. 3 SEM-EDS mapping of the 10CuNiCoA catalyst
- Fig. 4 Effect of reaction temperature on styrene conversion over the 10CuNiCoA catalyst
- Fig. 5 Effect of ternary catalysts in styrene oxidation using 5 mg catalysts and 1.5 mole equivalent of TBHP at 40°C after 24 h
- Scheme 1. Proposed reaction scheme for styrene oxidation catalyzed by the supported mixed nano-metal oxides

Supplementary Data:

1.CO chemisorption analysis

Fig. S1 XRD patterns of the (a) γ -Al₂O₃ (b) 30CuNiCoA and (c) 20CuNiCoA catalysts Table S1 TOF and carbon balance of styrene oxidation

Catalyst	BET Surface	Total Pore	Metal	
	Area (m^2/g)	Volume	Composition	
		(cm^3/g)	by ICP-OES	
			(Cu:Ni:Co) wt%	
γ-Alumina	263	0.84		
5CuNiCoA	213	0.64	3.23:1.58:0.55	
10CuNiCoA	200	0.59	6.56:3.41:0.96	
20CuNiCoA	172	0.51	13.05:6.43:2.01	
30CuNiCoA	153	0.44	16.98:8.25:2.57	

Table 1 Surface area and metal composition of the catalysts



Catalyst	Metal Dispersion*			Average Crystallite Size*		
	Cu	INI	Co	Cu	1N1	Co
10CuNiCoA	9	19	70	9.6	5.0	1.3
20CuNiCoA	7	21	67	13.9	4.7	1.5
30CuNiCoA	5	10	49	19.6	10.0	2.0

*calculated using CO chemisorption (more information in supplementary data)



Fig. 1 (a) N2 Adsorption-desorption isotherms and (b) pore size distribution of ternary catalysts



Fig. 2 (a,b,c) SEM and (d,e,f) TEM images of the 10CuNiCoA, 20CuNiCoA and 30CuNiCoA catalysts respectively



Fig. 3 SEM-EDS mapping of the 10CuNiCoA catalyst

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Fig. 4. Effect of reaction temperature on styrene conversion and selectivity to major products over the 10CuNiCoA catalyst



*Others: Acetophenone, Phenyl acetaldehyde

Fig. 5. Effect of ternary catalysts in styrene oxidation using 5 mg catalysts and 1.5 mole equivalent of TBHP at 40°C after 24 h



Scheme 1. Proposed reaction scheme for styrene oxidation catalyzed by the supported mixed nano-metal oxides



Graphical Abstract

Highlights:

- Supported Cu-Ni-Co oxides were synthesized with good dispersion of the metals
- > Ternary nanocatalysed approach was appropriate for styrene oxidation
- Catalysts stimulate direct oxidative cleavage of C=C bond to benzaldehyde
- > Enhancement in benzaldehyde selectivity is due to synergistic effect of metals

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