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Nanocatalysts for Low-Temperature Oxidation of CO: Review

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Abstract

The oxidation of CO covers a wide range of applications from gas masks, gas sensors, indoor air quality control to hydrogen purification for polymer electrolyte fuel cells. The reaction attracts renewed interest both in fundamental and applied research of catalysis and electrochemistry. Recent developments and trends in catalysis towards the synthesis of nanocatalysts for CO oxidation are discussed in this review. Different modifications made to conventional catalysts synthesis approaches for preparation of nanocatalysts are critically analyzed. Nanocatalysts developed on the basis of noble metals completely convert CO at temperatures below 0 ºC. The development of active and stable catalysts without noble metals for low-temperature CO oxidation is a significant challenge. It was found that Co_3O_4 nanorods can be steadily active for CO oxidation at a temperature as low as –77 ºC. High activity of catalysts at low temperatures connected with nanosize particles and high surface area. This review summarized main directions of nanocatalysts development for CO low temperature oxidation.

Introduction

Catalytic oxidation of CO is a known and commonly used process in the industry: clearing of exhaust gases of internal combustion engines, gaseous waste of petrochemical and metallurgical manufactures, generation of pure gases, CO oxidation for production of pure (without CO) hydrogen for proton-exchange membrane fuel cells. CO oxidation is an elementary step in many important industrial processes such as the production of methanol and the water-gas shift reaction [1, 2].

Low-temperature oxidation of CO, perhaps the most extensively studied reaction in the history of heterogeneous catalysis, is becoming increasingly important in the context of cleaning air and lowering automotive emissions. Low-temperature active oxidation catalysts are important in many applications. During the start of a cold car engine, CO and hydrocarbons are emitted untreated into the atmosphere. About 80–90% of all emissions from a car are released during the cold start [3-5]. CO is a toxic and detrimental air pollutant. It not only affects human beings but also vegetation and indirectly increases global warming. An estimate has shown that vehicular exhaust contributes about 64% of the CO pollution in developed countries. Due to the exponentially increasing number of automobiles on roads, CO concentrations have reached an alarming level in urban areas and regulatory measures had been adopted to curb the menace of vehicular pollution. Thus, the CO oxidation reaction is of practical importance for the control of the environmental pollution that results from combustion processes. To control vehicular exhaust pollution, end-of-pipe-technology using noble metal catalytic converters are recommended. The CO oxidation reaction over late transition metals has been the most widely studied surface catalyzed reaction. In general, the catalytic activity for the CO oxidation over transition metal surfaces is determined by the propensity of the metal surface to dissociate oxygen molecules and is counter balanced by the bond strength of the active oxygen species on the metal surface. The transition metals with

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half-filled d-bands reveal the highest activity, where the dissociation probability is not too low and the adsorption energy is not too high. Accordingly, Pt, Pd, and Rh are efficient metal catalysts, while Ru– due to its very high binding energy of oxygen – is a poor catalyst for the CO oxidation reaction. Noble metal catalysts are water tolerant but they usually require temperatures above 100 ºC for efficient operation [6, 7].

The increasing prices of noble metals with the increasing number of vehicles motivates the investigation of material concepts to reduce the precious metal content in automotive catalysts or to find a substitute for noble metals. Noble metal catalysts, usually require temperatures above 100 ºC for efficient operation. The development of active and stable catalysts without noble metals for low-temperature CO oxidation under an ambient atmosphere remains a significant challenge. One of the methods used for synthesis catalysts for CO oxidation are self-propagating high temperature synthesis (SHS) [8-13], Method and Solution combustion synthesis (SCS) method [14-19]. This review is devoted to last achievement in synthesis active catalyst for CO oxidation at low temperatures, especially nanocatalysts, which work at ambient temperature and bellow 0 ºC temperatures.

In recent years, increasing attention has been focused on the catalytic oxidation of carbon monoxide at ambient temperature due to its important applications in mine rescue devices for human safety, carbon dioxide lasers, proton exchange membrane fuel cells as well as many other applications in air purification devices, CO sensors, and even the burning of a cigarette. [20-23]. Low-temperature oxidation of CO, perhaps the most extensively studied reaction in the history of heterogeneous catalysis, is becoming increasingly important in the context of cleaning air and lowering automotive emissions.

Noble metals catalysts

Pt and Pd on CeO_2

Those results are better than on Pt catalysts produced by Solution Combustion Synthesis (SCS) method (50% CO conversion at 170 ºC) [24]. Ceria-supported Pt and Pd catalysts have been synthesized by the combustion method (the combustion mixture for the preparation of 1% Pt/CeO_2 contained $(NH_4)_2Ce(NO_3)_6$, H_2PtCl_6, and $C_2H_6N_4O_2$ (oxalyldihydrazide) in the mole ratio 0.99:0.01:2.33, (preheating temperature 350 ºC). Pt and Pd metals are ionically dispersed on the CeO_2 surface of crystallite sizes in the range of 15–20 nm. In 1% Pt/CeO_2 Pt is found to be in the C_2 and C_4 oxidation states whereas Pd is in the C_2 state in 1% Pd/CeO_2. The results of catalytic activities are compared with Pt and Pd metals dispersed on α-Al_2O_3 support prepared by the combustion technique. Both oxidation and reduction reactions occur at much lower temperatures over M/CeO_2 compared to those over M/Al_2O_3 (M = Pt, Pd). The rate and turnover frequency of $CO+O_2$ reactions over M/CeO_2 are higher than those over M/Al_2O_3. The observed enhanced catalytic activity of M/CeO_2 has been attributed to the ionic dispersion of Pt and Pd on CeO_2 leading to a strong metal–ceria interaction in the form of solid solution, $Ce_{1-x}M_xO_{2-(4-n)x/2}$, having linkages of the type $–O^{2-}–Ce^{4+}–O^{2-}–M^{n+}–O^{2-}(n=2,4)$ on the CeO_2 surface.

Pd/CeO_2

Pd/CeO_2 catalysts synthesized using the coprecipitation method under a wide range of palladium loading and calcinations temperatures were investigated [25]. The calculated amount of metallic palladium was dissolved in a minimum necessary amount of nitric acid; the resulting solution was cooled and supplemented with the calculated amount of cerium (III) nitrate. The reactant ratios were calculated so as to obtain the target Pd content in the catalyst in terms of non-aqueous supported Pd/CeO_2 sample. The Pd:Ce molar ratios of 1:99, 5:95 and 10:90 were prescribed in advance. It was found that the synthesis and subsequent calcinations at 450 ºC resulted in the formation of two main types of the catalyst components: PdO nanoparticles and $Pd_xCe_{1-x}O_{2-1}$ solid solution. Application of HRTEM allowed to establish the formation of aggregates where ceria or $Pd_xCe_{1-x}O_{2-1}$ nanoparticles were located around PdO nanoparticles. A subsequent calcination process resulted in partial dissolution of PdO nanoparticles in ceria lattice and formation of the surface compounds of palladium and ceria, PdO_x(s)/Pd–O–Ce(s), which contain high re-active oxygen according to the TPR-CO data. Based on the XPS and TPR-CO data the catalytic activity at low temperatures (<100 ºC) was determined by a combination of both palladium surfaces structures PdO_x(s)/Pd–O–Ce(s) and palladium ions Pd^{2+} in the $Pd_xCe_{1-x}O_{2-1}$ bulk phase. The best result was received on catalysts Pd/CeO_2 calcined at 600 ºC.

Tin-modified Pt/SiO_2

Low temperature oxidation of CO over alloy type $Sn–Pt/SiO_2$ catalysts with different Sn/Pt ratios has been investigated at different CO partial pressures using thermal programmed oxidation (TPO) technique and time on stream (TOS) experiments. The introduction of tin into platinum strongly increased the activity of the catalyst. The activity had a maximum, which depended on both the Sn/Pt (at./at.) ratio and the CO partial pressure. TOS experiments revealed the aging of the Sn–Pt/SiO_2 catalysts. FTIR and Mössbauer spectroscopy has been used to follow compositional and structural changes of Sn–Pt/SiO_2 catalysts during the catalytic run. The results show that the *in situ* formed, highly mobile “Sn–Pt” ensemble sites are responsible for high activity, while formation of relatively stable SnO_x type surface species are involved in the catalyst deactivation [26].

Ag/Fe_2O_3

Among the cheap transition metal oxides, Iron oxides and their composite oxides are also used as the catalysts and the catalyst carriers on CO oxidation [27]. Furthermore, it has been found that introduction of silver to the transition metal oxide systems strongly increased activity of the catalysts in the oxidation of CO [28-30]. The effect of impregnated Ag nanoparticles into Fe_2O_3 support in catalytic low temperature CO oxidation was investigated [31]. The nanocatalysts were prepared with a conventional impregnation method. It is clearly observed from the TEM images that the Ag nanoparticles are highly dispersed on the surface of Fe_2O_3 and are mostly around 5 nm in size. The results reveal that the catalytic activities increased significantly by increasing the Ag content, which causes a strong interaction with the Fe_2O_3. The catalytic activity clearly correlates with the Ag–Fe_2O_3 interaction. The experiments showed that the Fe_2O_3 supported silver catalyst has a good reproducibility and is highly stable for CO oxidation for a 50 h period of time even in the presence of high amounts of moisture and CO_2 in the feed gas. Best results (100% CO conversion at 200 ºC) were received on 20% Ag/Fe_2O_3.

Ag-Cu

$Cu_2Ag_2O_3$ has been prepared [32] by a precipitation method and evaluated for ambient (room) temperatures of carbon monoxide oxidation. The $Cu_2Ag_2O_3$ catalyst demonstrated appreciable activity and a relationship with preparation ageing time was observed. An ageing time of 4 h produced a catalyst with the highest oxidation performance.

Au nanoparticles

Au for long time was not considered as active catalyst for CO oxidation, but as was discovered in 1987 by Haruta et al. [33] it supported small Au nanoparticles (NPs) catalyze CO oxidation at or below room temperature.

Compared to a highly dispersed supported Pt catalyst, Au catalysts can be at a more active order of magnitude [34]. The attention arises not only from the commercial implication of this discovery, but also from the desire to answer the question of why the normally inert Au material can catalyze chemical reactions so effectively. A better understanding of the origin of the catalytic activity could lead to the discovery of other novel reactions. Gold exhibits a unique catalytic nature and action when it is deposited as nanoparticles on a variety of metal oxides. Most reactions are noticeably structure sensitive over such supported gold catalysts. Typical examples obtained in Japan at the low-temperature catalytic combustion, partial oxidation of hydrocarbons, hydrogenation of carbon oxides and unsaturated hydrocarbons, reduction of nitrogen oxides, and so forth, are presented. Gold exhibits high activity at low temperatures and superior stability under moisture, but only when deposited in nanoparticulate form on base transition-metal oxides [33, 35, 36] and elements of lanthanide series [37].

Au nanoparticles/on carriers

Au particles with a size of <5 nm supported on some metal oxides manifested a very high catalytic activity in oxidation of carbon monoxide at ambient temperatures. In succeeding years, the number of communications devoted to catalytic properties of nanosized Au particles has progressively increased, especially very rapidly from 1997 [38, 39]. Gold exhibits high activity at low temperatures and superior stability under moisture, but only when deposited in nanoparticulate form on base transition-metal oxides [33, 35, 36].

Precious metal catalysts based on supported gold have been widely used for the low temperature oxidation of CO with the precious metal deposited as nanoparticles on metal oxides [23, 40-42].

Another line of advance is also introduced in the thin films of gold – metal oxide composites, which are applicable to electrical and optical gas sensing [43]. Novel gold catalysts were prepared by coprecipitation from an aqueous solution of $HAuCl_4$ and the nitrates of various transition metals. Calcination of the coprecipitates in air at 400 ºC produced ultrafine gold particles smaller than 10 nm which were uniformly dispersed on the transition metal oxides. Among them, Au/α – Fe_2O_3, Au/Co_3O_4 and Au/NiO were highly active for H_2 and CO oxidation, showing markedly enhanced catalytic activities due to the combined effect of gold and the transition metal oxides. For the oxidation of CO they were active even at a temperature as low as −70 ºC [44].

Experimental and theoretical studies on the catalytic properties of oxide supported Au NPs have suggested thus far that the size of Au NPs [45-48], their structural fluxionality [49-51], their electronic interaction with supporting materials [52, 53], and the presence of a Au NP−support interface [54, 55], are factors that activate supported Au NPs.

A dramatic breakthrough in the heterogeneous catalysts of Au came when gold could be deposited on metal oxides as nanoparticles through coprecipitation [44] and deposition-precipitation methods [56]. Since then, many reactions over supported gold catalysts have been found to be noticeably structure sensitive. It is commonly known that the catalytic activity of gold nanoparticles in CO oxidation is strongly dependent on the support nature [57-59]. Previous comparative studies showed that the activity of supported gold catalysts depends, sensitively, on the support materials [36, 60, 61].

The selection of metal oxide supports the control of the size of Au particles, and the designing of the contact structure of the Au–metal oxide interface allow to tune the nature and activity of supported gold catalysts in a wide range. In order to clarify the support effect on CO oxidation over Au catalysts without the influence of the size effect of Au, Au was deposited on a variety of supports with high dispersion by gas-phase grafting (GG) of an organo-gold complex. Comparison of Au/SiO_2 with Au/Al_2O_3 and Au/TiO_2, which were prepared by both GG and liquid-phase methods and were active for CO oxidation at 0 ºC, showed that there were no appreciable differences in their catalytic activities as long as Au is deposited as nanoparticles with strong interaction. However, Au deposited onto the acidic supports, such as silica–alumina and activated carbon (AC), exhibited a much lower CO oxidation catalytic activity than those of the active Au catalysts, such as Au/TiO_2 [62]. Among the gold catalysts supported on TiO_2, α-Fe_2O_3, and Co_3O_4 the turnover frequencies for CO oxidation per surface gold atom are almost independent of the kind of support oxides used and increase sharply with a decrease in diameter of gold particles below 4 nm. Small gold particles not only provide the sites for the reversible adsorption of CO but also appreciably increase the amount of oxygen adsorbed on the support oxides. In the temperature range −10 ºC to 65 ºC, the activation energies for CO oxidation were 8.2 kcal/mol (Au/TiO_2), 8.4 kcal/mol (Au/α-Fe_2O_3), and 3.9 kcal/mol (Au/Co_3O_4) [36] Findings (Hyun You Kim, 2012) on the mechanism of CO oxidation catalyzed by Au NPs supported on stoichiometric and partially reduced CeO_2, confirm a critical role of oxygen vacancy in the CeO_2 surface on CO oxidation activity of CeO_2-supported Au NP, providing a theoretical guideline on the design of highly reactive catalysis in the supported NP class for low temperatures of CO oxidation.

Most active catalysts were prepared by depositing gold onto first-raw transition metal oxides (TiO_2, Co_3O_4, Fe_2O_3, NiO) as well as onto $Be(OH)_2$ and $Mg(OH)_2$. Also, some composite oxide supports, such as $ZnFe_2O_4$, $NiFe_2O_4$, $MgFe_2O_4$ [63] were investigated. These catalysts were studied in sufficient detail but, for different reasons, they are not suitable for large-scale applications. From the practical point of view, alumina would be preferable support for Au catalysts as compared with other metal oxides.

Au/Al_2O_3

In work [64] preparation and catalytic properties of nanodispersed Au/Al_2O_3 catalysts for low-temperature CO oxidation were described. The catalysts with a gold loading of 1–2 wt.% were prepared via deposition of Au complexes onto different aluminas by means of various techniques (‘‘deposition-precipitation’’ (DP), incipient wetness, ‘‘chemical liquid-phase grafting’’ (CLPG), chemical vapor deposition (CVD)). Au particle sizes vary from 1 to 18 nanometers depending on the method of preparation. Using the hydroxide or chloride gold complexes capable of chemical interaction with the surface groups of alumina as the catalyst precursors (DP and incipient wetness techniques, respectively) produces the catalysts that contain metallic Au particles mainly of 2–4 nm in diameter, uniformly distributed between the external and internal surfaces of the support granules together with the surface ‘‘ionic’’ Au oxide species. Regardless of deposition techniques, only the Cl-free Au/Al_2O_3 catalysts containing the small Au particles ($d \leq 5$ nm) reveal the high catalytic activity toward CO oxidation under near-ambient conditions, the catalyst stability being provided by adding the water vapor into the reaction feed. Best results were received on 1.5% Au/$\delta - Al_2O_3$ catalysts, on which CO conversion was 95% at 0 ºC (feed stream composition: 1% CO, 2.4% H_2O and 20% O_2 in N_2; GHSV, 60,000 h^{-1}). For the purpose of comparison, industrial catalysts 2.3% Pt/(δ-Al_2O_3 + β-zeolite) have 100% CO conversion at 100 ºC. Regardless of the deposition technique (DP, IMP or CVD), the small Au particles ($d \leq 5$ nm) deposited onto γ – and $\delta - Al_2O_3$, which are free of Cl- impurity, are highly active toward catalytic combustion of CO in wet air stream under near-ambient conditions.

Generally, the Au/Al_2O_3 catalysts prepared by DP demonstrate the highest activity in CO oxidation as compared with the CVD or impregnated catalysts, probably, due to the smaller mean Au particle diameter and narrower size distribution.

Au-MO_x/Al_2O_3

Composite oxide MO_x/Al_2O_3 supported gold catalysts for low-temperature CO oxidation were prepared and investigated [65].The presence of transition metal oxide was proved to be beneficial to the improvement of catalytic performance of Au/Al_2O_3 catalysts for low-temperature CO oxidation. On $Au/FeO_x/Al_2O_3$ catalyst 100% conversion is at – 50 ºC, on Au/Fe_2O_3 at – 22 ºC, on Au/Al_2O_3 at 15 ºC. The $Au/MO_x/Al_2O_3$ (M = Fe, Co, Mn, Cu) catalysts are more active than Au/Al_2O_3 catalysts. HDP is more suitable to prepare gold catalysts for commercial applications. From the characterizations of an $Au/FeO_x/Al_2O_3$ catalyst, it seems reasonable that for developing high catalytic activity, the gold catalyst should have minor portion oxidized gold species and the transition metal oxide supports should be amorphous which can result in synergistic effects between gold and supports. One possible pathway for CO oxidation on $Au/FeO_x/Al_2O_3$ catalyst is that the CO adsorbed on gold particles reacts with adsorbed oxygen, which is possible to occur on oxygen vacancies on the support or at the metal–support interface. The presence of gold as small particles appear to be crucial for the high-activity [66, 67].

Au/Fe_2O_3

Haruta et al. [36, 44] firstly demonstrated active Au/Fe_2O_3 catalysts for room temperature CO oxidation. Both heat-treated and untreated Au/Fe_2O_3 catalysts were found to exhibit low temperature activity toward CO oxidation, with untreated samples being much more active, though the heat-treatment could control the catalytic activity for CO oxidation [68-72]. The deposition–precipitation method was shown to produce more active Au/Fe_2O_3 catalysts than conventional coprecipitation [70-73]. Hutchings and co-workers [74] prepared an Au/Fe_2O_3 catalyst using a two-stage calcinations procedure for the competitive oxidation of dilute CO in the presence of moist excess H_2 and CO_2, achieving target conversion and selectivity.

Au-Fe-La-O

La_2O_3 doped Fe_2O_3 support was prepared by coprecipitation method, and gold was loaded by deposition-precipitation. Thermal stability of gold catalyst was enhanced considerably by La_2O_3 doping. Even when calcined at 500 ºC for 12 h, the catalyst doped with La_2O_3 could convert 90% of CO at 28.9 ºC, while the catalyst without La_2O_3 doping achieved 90% CO conversion at 43.5 ºC [75]. After calcination at 500 ºC, the size of gold particles in Au/Fe_2O_3 was in the range of 6–10 nm and the size of support grains was 50–100 nm. However, the sizes of gold particles and support grains in $Au/La_2O_3/Fe_2O_3$ were remained in the ranges of 4–8 nm and 25–50 nm, respectively. The results of X-ray diffraction and thermal analysis also proved that La_2O_3 doping not only restrained the growth of gold particles, but also retarded the crystallization of support.

Au/C

Activated carbon (AC) supports have been seldom used for gold deposition in spite of the advantages of the AC compared to oxide supports such as a high specific surface areas of up to 3000 m^2/g, high stability in acidic and basic media [76], and easy recovery of supported metals by burning off the catalyst. Prati et al. [77, 78] showed that the Au/AC catalysts are active in different liquid-phase reactions, but the activities of these catalysts are sensitive to the preparation method. Gold nanoparticles of 2–5 nm supported on woven fabrics of activated carbon fibers (ACF) were effective during CO oxidation at room temperature. To obtain a high metal dispersion, Au was deposited on ACF from aqueous solution of ethylenediamine complex $[Au(en)_2]Cl_3$ via ion exchange with protons of surface functional groups. The temperature-programmed decomposition method showed the presence of two main types of functional groups on the ACF surface: the first type was associated with carboxylic groups easily decomposing to CO_2 and the second one corresponded to more stable phenolic groups decomposing to CO [79]. It was found that Au catalysts on CeO_2 [80-85] and ZrO_2 [86-89], are very active catalyst of CO oxidation at low temperatures.

The $Au/Ce_{1-x}Zr_xO_2$ (x = 0, 0.25, 0.5, 0.75, 1) catalysts were synthesized by the direct anionic exchange (DAE) method and tested in CO oxidation [90]. Poisoning effect of residual chlorine on their catalytic performance was found. The agglomeration of Au particles during the calcination step in the presence of residual chlorine was observed. Its removal through the washing treatment both inhibited the sintering process and led to the increase in activity of the studied systems. The sequence of increasing activity was followed by the sequence of increasing reducibility of the catalysts. This shows the role of the support redox properties in the creation of the catalytic performance of supported Au nanoparticles in CO oxidation.

Non-noble catalysts

CuO

Copper oxide [91-93] and supported copper oxides [21, 94-101] are known to be highly active for CO oxidation, however, usually at elevated temperatures (>200 ºC). Most of the studies on copper based systems have been on supported copper oxides, among which are CuO/CeO_2 [94-98], $CuO/Sm\text{-}CeO_2$ [21], CuO/ZrO_2 [99], CuO/ThO_2 [100] and CuO/Al_2O_3 [101]. There are however, only very few studies on unsupported copper oxide for this important reaction. Room temperature oxidation of carbon monoxide to carbon dioxide has been achieved for the first time over unsupported copper oxide catalysts prepared by a controlled heating of precipitated copper hydroxide after activation of the catalyst in a redox environment [102].Carbon monoxide oxidation has been studied over different oxides of copper as well as a copper oxide sample obtained from precipitation. It is found that drying and calcination of the precipitated hydroxide are crucial parameters that affect the catalyst performance dramatically. Experimental results indicate that the active phase is a metastable non-stoichiometric form of copper oxide formed during the treatment of the oxide in a redox environment. Mixed oxides such as $CuMnO_4$ [103] and CuO-ZnO [104-106] have been reported as active catalysts for CO oxidation at ambient temperature. Here are some examples of active nanocatalysts on the base of copper oxide on carrier presented.

CuO/MeO-SiO$_2$

The promotional effects of CeO_2, MnO_2 and Fe_2O_3 on CuO/SiO_2 were studied in CO oxidation reactions. The CO oxidation test showed that CeO_2 had the most promoting effects and $CuO/CeO_2–SiO_2$ realized complete conversion of CO at 150 ºC, which is 120 ºC lower than that of reference catalyst CuO/SiO_2, because addition of CeO_2 formed more Cu + species and moveable lattice oxygen species on the surface of the catalysts. The order of promoting effects for various added oxides is $CeO_2 > MnO_2 > Fe_2O_3$. The characterization results proved that the Cu + species and oxygen mobility played a very important role in CO oxidation [107].

Cu-Mn-O

Hopcalite catalysts (mixtures of manganese and copper oxides ($CuMn_2O_4$)) were originally developed for purifying air in submarines, but they are not especially active at ambient temperatures and are also deactivated by the presence of moisture [108, 109]. Due to the complexity of the preparation methods of hopcalite, attempts have not stopped to find new preparation methods for more active hopcalite. Copper-manganese oxide catalysts prepared by co-precipitation was described by Taylor and coworkers [110, 111]. They showed that the effect of a broad range of precipitation parameters, such as ageing time, ageing pH, ageing temperature, copper/manganese molar ratio and calcinations temperature are of crucial importance in controlling the catalytic performance of CO oxidation at ambient temperature. The effect of the preparation conditions of a hopcalite (coppermanganese oxide) catalyst are investigated for the oxidation of carbon monoxide at ambient temperature. In the present study the hopcalite is prepared by coprecipitation from an aqueous solution of copper and manganese nitrates [110, 112]. The activity of hopcalite materials is principally affected by two features, namely the surface area and the phase composition. Both of these features are controlled principally by the conditions used for the calcination that is required to activate the precursor, formed initially from coprecipitation. High activity is observed for materials that retain high surface area and are not crystalline. In [113] 60% CO conversion reached at 27 ºC on hopcalite catalyst.

Cu-Fe-O

Even copper iron composite oxide catalysts were prepared by coprecipitation, ball-milling, thermal solid–solid interaction, and sol–gel method [114-118] and few were studied at low temperature CO oxidation. It is still a challenge to develop high surface area and porous $CuO–Fe_2O_3$ composite materials for the anticipation of enhancing catalytic performance. A series of mesoporous $CuO–Fe_2O_3$ composite oxide catalysts with different CuO contents were prepared by a surfactant-assisted method of nanoparticle assembly [119]. These mesoporous $CuO–Fe_2O_3$ catalysts possess a wormhole-like mesostructure with a narrow pore size distribution and high surface area, exhibiting high catalytic activity and stability for low-temperature CO oxidation. The catalytic behavior depended on the CuO content, the precalcination temperature, the surface area and the particle size of the catalysts. Catalyst 50% CuO–50% Fe_2O_3, which is of amorphous nature and has the highest surface area(3–4 nm, surface area of 299 m^2/g), exhibits the highest catalytic activity of the total CO oxidation temperature at 110 ºC.

Cu-Zn-O

Copper/zinc mixed oxide catalysts have been prepared using co-precipitation by varying the ageing time in the precipitation liquor [120]. The catalysts were studied for the oxidation of CO at ambient temperature. All the catalysts exhibited appreciable CO oxidation activity. It is shown that the ageing time is important in controlling the catalytic activity. The most active catalysts were aged for 165 min. Correcting catalyst activity for the effect of surface area demonstrated that catalysts aged <60 min had the greatest oxidation rates. The calcined catalysts were all comprised of CuO and ZnO. The origin of the high activity for the CuO/ZnO catalysts prepared with short ageing times is not clear, but it appears that, the highly dispersed CuO and ZnO, and the presence of solid solution phases formed during the controlled precipitation and ageing process are important.

Cu-Zn-Ce-O

Copper-zinc oxide catalyst is prepared by co-precipitation technique [121]. The effects of aging the precipitate in the parent solution and addition of CeO_2 are investigated. CuO-ZnO catalyst containing 60% CuO and 40% ZnO is found to be active for the ambient temperature oxidation of CO; however the activity can be improved considerably by aging the catalyst during the precipitation process. Alternatively, the catalyst activity can be improved by the addition of CeO_2 during the precipitation without aging the precipitate. X-ray photoelectron spectra (XPS) and XRD results show that aging the catalyst during the precipitation process brings out more ZnO to the surface leading to higher CuO dispersion. This leads to the formation of relatively less crystalline or amorphous CuO that promotes the formation of more linear or weakly bonded CO on the catalyst surface as well as the creation of CuO_x species under redox conditions. The metastable copper oxide species is a good electrophilic reagent with superior oxygen transfer capacity and the presence of weakly bonded surface CO ensures a low temperature oxidation activity for the catalyst. It is further seen that addition of ceria to the catalyst also brings out similar advantages. However, increase in the CeO_2 content increases the CO bonding strength causing an increase in the light-off temperature (loss of low temperature oxidation activity), in spite of high overall reducibility and CO adsorption capacity of the catalyst. The reducibility and susceptibility to variation in the oxidation states of copper oxide are critical to the activity of the catalyst. It is also found that addition of CeO_2 brings out a significant improvement in the catalyst stability over an extended reaction period as well as at elevated reaction temperature. In a nutshell, the main factors responsible for the superior performance of the catalysts appear to be: the surface morphology, the dispersion of copper oxide, the redox properties of the oxide and the ability to achieve a partially reduced state of copper oxide phase at the interface.

Cu-Ce-O

Metal-ceria systems are several orders of magnitude more active than other oxide supported catalysts for various redox reactions because of the high oxygen storage capacity and reducibility of ceria. The CuO/CeO_2 system is a promising catalyst for CO oxidation, because it has a specific activity that is several orders of magnitude higher than that of conventional Cu-based catalysts and which is comparable or even superior to the activity of Pt-based catalysts [94, 95, 122-124]. Cu–Ce–O composite catalysts have received considerable attention for CO oxidation in recent years [98, 125-130]. The $Ce_{20}Cu_5O_x$ sample exhibited poor catalytic performance for CO oxidation in comparison with the other catalysts, and showed complete CO conversion at 110 ºC. It can be observed that the addition of a small amount of Ni led to a large increase in the catalytic activity for the reaction at low temperature. With increasing nickel content, the catalytic activity was initially increased and attained a maximum when the Cu/Ni atomic ratio was 5:0.4. However, with a further increase in nickel content, the catalytic activity decreased. The $Ce_{20}Cu_5Ni0.4O_x$ catalyst presented the highest catalytic activity for CO oxidation. Its temperature at which the complete oxidation of CO occurred was lower than those for the other catalysts, and it showed complete CO conversion at 70 ºC. A urea combustion method or SCS was used for the preparation of the Cu–Ce–O nanocatalyst without the need for a binder or additional calcination steps [131]. The catalytic performance of the catalyst for preferential oxidation of CO was investigated under dry and humid feed gas conditions, and the catalyst was also examined for CO removal at the operating temperature of the PEMFC anode. A 99.3% CO conversion CO conversion and 75% selectivity for CO_2 could be achieved at 130 ºC in the presence of H_2O and CO_2. CeO_2 nano-crystals were synthesized by a sol–gel process and then used as support for CuO/CeO_2 (sol–gel) catalysts prepared via the impregnation method [132]. XPS analysis indicated the presence of reduced copper species in the CuO/CeO_2 catalysts. TPR showed that there are different copper species in the catalysts. The influence of calcination time, temperature and CuO loadings on the catalytic activity of CuO/CeO_2 catalysts has been studied. The CuO/CeO_2 (sol–gel) catalysts exhibited higher catalytic activity (100% CO conversion at 90 ºC) than the CuO/CeO_2 (commercial) catalysts. The difference in CeO_2 particle size, morphology and surface area affected the dispersion of CuO on the catalysts, which was responsible for the difference in their catalytic activity. The sol–gel combined with the impregnation method appears to be a simple and effective method for the preparation of CuO/CeO_2 catalysts.

SCS CuO promoted CeO_2–M_xO_y (M = Zr, La, Pr and Sm) catalysts

A series of copper oxide promoted CeO_2–M_xO_y (M_xO_y = ZrO_2, La_2O_3, Pr_2O_3 and Sm_2O_3) mixed oxides were synthesized by a microwave-assisted solution combustion method using urea as the fuel and the respective metal nitrates as the precursors. XPS studies confirmed the presence of cerium in both Ce^{3+} and Ce^{4+} oxidation states in all mixed oxides. All the doped mixed oxides exhibited better CO oxidation activity compared to the undoped copper–ceria catalysts. The significance of the combustion synthesis method has been in that it includes simplicity, flexibility and the control of different favorable factors. All the doped catalytic materials showed an improvement in the CO oxidation activity compared to the Cu/CeO_2 catalyst. Among all the catalysts, Zr^{4+} doped Cu/CeO_2 exhibited excellent catalytic performance followed by Sm^{3+}, Pr^{3+} and La^{3+}-doped Cu/CeO_2 catalysts. 100% of CO conversion was achieved by the microwave assisted SCS synthesis 5 wt.% Cu/CeO_2–ZrO_2 100 ºC [19].

A glycine-nitrate approach of SCS method was used for the synthesis of Co/CeO_2 nanoparticle for preferential oxidation of CO. A precursor solution was prepared by mixing glycine with an aqueous solution of blended nitrate in stoichiometric ratio [18]. Then the glycine-mixed precursor solution was heated in a beaker for producing nanosized porous powders. Catalytic properties of the powders were investigated and results illustrate that the Co-loading of 30 wt.% catalysts exhibit excellent catalytic properties (100% CO conversion at 150 ºC). It is also found that the optimal Co and Ce ratio is essential to obtaining a good catalyst, and excess cobalt loading can lead to the decrease in catalytic activity due to the poor dispersion of active species. The Co/CeO_2 prepared by glycine-nitrate combustion method (SCS) with optimum element component and precondition shows the excellent catalytic properties for CO oxidation reaction, which is ascribed to the high dispersity and good reducibility of Co_3O_4 as well as the formation of hexagonal Co/CeO_2 via Ce-Co interaction. The SCS method was found to be a simple, fast and effective method for the preparation of catalysts.

Cu-Ce-Ti-O

A series of $CuO/Ce_{1-x}Ti_xO_2$ catalysts used for low-temperature CO oxidation were prepared by impregnation with the support derived from surfactant-assisted co-precipitation. It is found that the support CeO_2, prepared by the surfactant-assisted method, possesses a much larger specific surface area than the one obtained from conventional precipitation [133]. Doping Ti in the support with Ti/Ce atomic ratio of 1:9 or 3:7 can further increase the surface area of CeO_2 and decrease its crystallite size. As a result, the active Cu species possess higher dispersion on the support $Ce_{1-x}Ti_xO_2$ than on pure CeO_2. The strong interaction between the dispersed Cu species and the support $Ce_{1-x}Ti_xO_2$ makes the catalysts possess much higher oxidation activity and thermal stability. Ti doping in the support CeO_2 can further increase its surface area and decrease the crystallite size of CeO_2 due to the formation of Ti–Ce oxide solid solution. However, the atomic ratio of Ti/Ce is sensitive to the dispersion of Cu species and its reducibility. The proper ratio of Ti/Ce should be 1:9 or 3:7, which ensures the presence of a more highly dispersed copper species strongly interacting with CeO_2, and therefore enhances the oxidation activity of the catalysts. The best result received by the $CuO/Ce_{0.7}Ti_{0.3}O_2$ catalyst: 100% CO conversion at 80 ºC.

Ni promoted CuO/CeO_2

In CeO_2, the facile Ce^{4+}/Ce^{3+} redox couple gives a high oxygen storage capacity (OSC) by the reversible addition and removal of oxygen in the fluorite structure of ceria. It has been observed that the redox property of $Ce_{1-x}MO_y$ solid solutions, formed by incorporating other metal ions into CeO_2, is better than that of CeO_2 alone. This suggested the use of Ni^{2+} cations with a smaller size that can be incorporated into the cubic lattice to form a solid solution and help the change of Ce^{4+} to Ce^{3+}. In addition, it is also possible that Cu ions can have a more facile redox behavior during oxidation and reduction oscillations from the introduction of NiO. A series of $Ce_{20}Cu_5Ni_yO_x$ catalysts for CO oxidation at low temperature was prepared [134]. $Ce_{20}Cu_5Ni_yO_x$ catalysts with different nickel contents were prepared by the reverse coprecipitation method, which is a long, multistage process: $Cu(NO_3)_2 \cdot 3H_2O$, $Ce(NO_3)_3 \cdot 6H_2O$, and $Ni(NO_3)_2 \cdot 6H_2O$ were used as sources of Cu, Ce, and Ni, respectively. A mixed solution of weighed quantities of copper nitrate, cerium nitrate, and nickel nitrate was added to a solution of sodium hydroxide at a rate of 3–4 ml/min under vigorous stirring at 60 ºC. The pH value was adjusted to 9.7–10 with sodium hydroxide to produce a precipitate suspension. Then, a small amount of L-glutamate sur-factant was added to the suspension after 5 min. The precipitate obtained was aged at 60 ºC for one hour under stirring and then filtered and washed with hot distilled water several times to remove excess ions, followed by drying at 110 ºC for 4 h. The dried material was crushed and calcined in air at 350 ºC for 3 h to give the final powder $Ce_{20}Cu_5Ni_yO_x$ catalyst. $Ce_{20}Cu_5Ni_{0.4}O_x$ exhibited the highest catalytic activity. The addition of NiO increased the amount of copper ions doped into the CeO_2 matrix and gave more oxygen vacancies in ceria by the formation of a Ni-O-Ce solid solution. XPS results showed that large quantities of Cu^+, Ce^{3+}, and lattice oxygen existed in the fresh $Ce_{20}Cu_5Ni_{0.4}O_x$ catalyst. Cu^+ ions in the catalyst can easily migrate to the ceria lattice to form a Cu-O-Ce solid solution, which enhance the release of the lattice oxygen of the oxides under a reducing atmosphere. The high catalytic activity of $Ce_{20}Cu_5Ni_{0.4}O_x$ is due to the promoter giving increased amounts of Cu^+ in the catalyst and the formation of solid solutions of both Cu-O-Ce and Ni-O-Ce.

Co_3O_4

Cobalt oxide (Co_3O_4) is very attractive for the preparation of oxidation catalysts because of the presence of mobile oxygen in Co_3O_4 [135-140]. The high activity of Co_3O_4 on CO oxidation is likely to be due to the relatively low ΔH of vaporization of O_2 [141, 142]. This means that the Co–O bond strength of Co_3O_4 is relatively weak, so reactive oxygen can easily be obtained from the lattice oxygen. Thus, many researchers have measured the catalytic activity of Co_3O_4 for CO oxidation [143].

Among the metal oxides, tricobalt tetraoxide is the most active for CO oxidation [144, 145], but is severely deactivated by trace amounts of moisture (about 3–10 parts per million, p.p.m.) that are usually present in the feed gas. In fact, under dry conditions with a moisture content below 1 p.p.m., which can be obtained by passing the reaction gas through molecular-sieve traps cooled to dry-ice temperature, Co_3O_4 is intrinsically active for CO oxidation [146, 147] even below a temperature of –54 ºC. However, in normal feed gas, most of the active sites of Co_3O_4 are covered by H_2O so the adsorption of CO and oxygen is appreciably hindered.

In [148] it is reported that tricobalt tetraoxide nanorods not only catalyse CO oxidation at temperatures as low as –77 ºC but also remain stable in a moist stream of normal feed gas. High-resolution transmission electron microscopy demonstrates that the Co_3O_4 nanorods predominantly expose their {110} planes, favouring the presence of active Co^{3+} species at the surface. Kinetic analyses reveal that the turnover frequency associated with individual Co^{3+} sites on the nanorods is similar to that of the conventional nanoparticles of this material, indicating that the significantly higher reaction rate that obtained with a nanorod morphology is probably due to the surface richness of active Co^{3+} sites. These results show the importance of morphology control in the preparation of base transition-metal oxides as highly efficient oxidation catalysts. Nanorod-shaped Co_3O_4 was prepared by the calcination of a cobalt hydroxide carbonate precursor obtained by the precipitation of cobalt acetate with sodium carbonate in ethylene glycol. When cobalt acetate was mixed with ethylene glycol at 160 ºC, the $–OCH_2–CH_2O–$ chain was tightly bound with the cobalt cations. The addition of aqueous sodium carbonate solution resulted in the formation of a solid cobalt hydroxide carbonate incorporating ethylene glycol, having a nanorod-shaped structure with a diameter of 10–20 nm and a length of 200–300 nm. Subsequent calcination of this precursor at 450 ºC in air caused a spontaneous transformation of the morphology, forming Co_3O_4 nanorods with diameters of 5–15 nm and lengths of 200–300 nm. The CO oxidation reaction was performed in a continuous-flow fixed-bed quartz reactor under atmospheric pressure. A 200 mg (40-60 mesh) sample was loaded and pre-treated with a 20 vol.% O_2/He mixture (50 ml min^{-1}) at 450 ºC for 30 min. After cooling to –77 ºC, a 1.0 vol.% CO/2.5 vol.% O_2/He mixture (50 ml min^{-1}) was introduced. Dry conditions were obtained by passing the feed gas through a molecular-sieve trap cooled to dry-ice temperature. Kinetic measurements were conducted at –86 to –56 ºC with feed streams of 0.5–1.2 vol.% CO and 1.0–5.1 vol.% O_2 balanced with He, and the CO conversions were adjusted to below 15% by varying the hourly gas space velocity to calculate the reaction rates under differential reactor conditions.

The nanocrystalline Co_3O_4 catalysts were prepared [149] via wet-chemical precipitation and dry-solid-state reaction, respectively. To assess the suitability of such Co_3O_4 as an oxidation catalyst, CO oxidation was taken as model reaction. The best catalyst was obtained by a dry grinding route calcined at 300 ºC, showing the 50% conversion of CO at −92 ºC, under a stream of normal feed gas containing moisture. Comparing the reaction rate per cobalt oxide mass unit at room temperature (ca. 1.53 mmol g^{-1} s^{-1}) with the Au-based catalyst in the current literature confirmed the exceptionally high activity of these new materials.

A nanocrystalline cobalt oxide (Co_3O_4)-based catalyst formed by heating a basic cobalt(II) carbonate precursor in air at 250–300 ºC has been shown to exhibit much greater catalytic activity than Co_3O_4 calcined at higher temperatures [150]. In a highly exothermic reaction, the properly calcined catalyst rapidly oxidizes carbon monoxide to carbon dioxide at room temperature. The observation of a CO band at 2006 cm^{-1} (FT-IR) indicates that CO is adsorbed onto cobalt atoms in a low oxidation state. The highest catalytic activity appears to be achieved when a specific ratio of Co(II) to Co(III) is found on the surface and the particle size is small (i.e., the surface area is large).

Co_3O_4/Al_2O_3

Alumina-supported Co_3O_4 was reported to give 50% CO conversion at –63 ºC for a normal feed gas, but the CO conversion was obtained with a transient method [151] not at steady state. Co_3O_4 nanorods can be steadily active for CO oxidation at a temperature as low as –77 ºC, giving 100% CO conversion, and are quite stable even under a stream of normal feed gas containing moisture [148].

Co_3O_4-CeO_2

The modification of ceria (CeO_2) on high surface area cobalt oxide (Co_3O_4) and the promotion effect of CO oxidation via different pretreatment conditions were studied. The high-valence cobalt oxide was prepared first by precipitation-oxidation, followed by reduction at 230 ºC to get a pure and high surface area of cobalt oxide (S = 100 m^2 g^{-1}). Further, the Ce-Co catalyst was prepared by impregnation with cerium nitrate (20% cerium loading) on Co_3O_4. Pretreatment of Ce-Co catalyst was divided into two methods: reduction (under 200 and 400 ºC) and calcination (under 350 and 550 ºC). The results showed that pretreatment under low-temperatures obtained both larger surface area and better activity. The Ce-Co catalyst exhibited the best catalytic activity in CO oxidation with T50 (50% conversion) at 88 ºC, T100 at 130 ºC among a series of catalysts due to the combined effect of cobalt oxide and ceria. The optimized pretreatment of CeO_2/Co_3O_4 catalysts can clearly enhance the catalytic activity [152].

Cu-Cr-O

Many works [153-155] reported that copper chromite is the best-suited catalyst for CO oxidation. Shelef et al. [154] reported that copper chromite is the best-suited catalyst for this reaction among the series: $CuCr_2O_4 > Co_3O_4 > Fe_2O_3 > MnO > NiO > Cr_2O_3 > V_2O_5$. Solovev and Orlik [156] compared the copper chromite with other catalysts and arranged them by order of decreasing activity: $CuCr_2O_4 > CuCo_3O_5 > Co_3MnO_6 > CuMnO_3$. Stegenga et al. [157] reported that Cu-Cr oxide-based converters are superior to precious metal-based devices for CO oxidation. Murthy and Ghose [158] studied oxidation of CO on Mg- and Al-substituted $CuCr_2O_4$ spinel catalysts at atmospheric pressure and temperatures between 100–450 ºC and found the best mass activity for an un-substituted $CuCr_2O_4$. The activity of $CuCr_2O_4$ catalysts is noticeably higher than that of individual oxides; complete CO oxidation on the catalyst was reached at 157 ºC, which shows the synergetic effect between copper and chromium in the mixed oxides. Thus, among non-noble metals, copper chromite is found to be most promising and exhibits comparable activity for CO oxidation to that of precious metals. Further, low cost, easy availability and advance synthesis methods with stabilizer, promoter, etc. advocates for the use of copper chromite as an auto exhaust purification catalyst. There is a lot of literature available on copper chromite catalysts for CO oxidation [159] including SHS Cu-Cr-O catalysts [12, 160]. It can be proposed to thoroughly investigate unsupported as well as supported $CuCr_2O_4$-CeO_2 nano-sized catalysts for future applications of CO oxidation.

Fe-Co nanocatalysts

There are many methods to prepare nano-sized Fe-Co mixed oxide, such as mechanical milling [161, 162], water-in-oil microemulsions [163, 164], bubbling oxygen [165], co-precipitation using microwave heating [166], hydrothermal methods [167], sol gel-like technique [168] simple co-precipitation in an aqueous solution [169], and mechanochemical [162]. Among all of the above mentioned methods, co-precipitation in aqueous solutions is the simplest and most compatible one under industrial conditions in order to prepare large amounts of mixed oxides, but even this method is long and multi-stage. For example, in [27, 170] low temperature CO oxidation over iron–cobalt mixed oxide nanocatalysts with different Co/Fe molar ratios was investigated. The nanocatalysts were prepared with a facile coprecipitation method. Mixed oxides containing iron and cobalt catalysts were provided by the coprecipitation method. In a typical preparation, firstly, $Fe(NO_3)_3 \bullet 9H_2O$ (Merck, 98%) and $Co(NO_3)_2 \bullet 6H_2O$ (Merck, 99%) with different molar ratios were dissolved in distillated water and the resulting solution was heated to 70 ºC. Then an aqueous solution of sodium carbonate (0.5 M) was added to mixed nitrate solution under continuous stirring at a rate of 2–3 ml/min at 70 ºC until pH 7.0 was achieved. The resulting precipitate was aged at pH of 7.0 for 2 h and then filtered and washed with warm distilled water several times for removing excess ions. Afterwards, the precipitate was dried in air at 110 ºC for 16 h and finally calcined at 400 ºC in air atmosphere for 6 h with a ramp rate of 3 ºC/min. The feed gas for oxidation contained 4% CO, 20% O_2 and 10% N_2 balanced with He at gas hourly space velocity (GHSV) of 60,000 ml/g h. Prior to measurements, catalysts were pretreated in 20% O_2 balanced with He, at 200 ºC for 2 h. The activity tests were carried out at different temperatures, ranging from 25 to 325 ºC. The catalytic results showed that the addition of Co to iron oxide even in small amounts had a dramatic effect on increasing CO conversion at lower temperatures. Results showed that for a given temperature, the conversion of CO decreased with an increase in GHSV, and the activity and stability of catalysts with introducing different feed compositions at 100 ºC are almost alike, but it can be seen that at temperature of 130 ºC, an increase in the O_2/CO ratio led to the increase of the CO conversion on the Fe–Co catalyst, regardless of the CO concentration. This study shows that the stability of Fe–Co catalysts increases with the increase in the reaction temperature.

Mn-Ce-Me nanocatalysts

$Mn_{0.5}Ce_{0.5}O_2$ and $Me/Mn_{0.5}Ce_{0.5}O_2$,(Me=Cu, Ag) catalysts were produced by the precipitation method. A 100% CO conversion was achieved on CeO_2 is at 210 ºC, on MnO_x at 120 ºC, on $Mn_{0.5}Ce_{0.5}O_2$ at 92 ºC, on Cu /$Mn_{0.5}Ce_{0.5}O_2$ at 77 ºC, on Ag/$Mn_{0.5}Ce_{0.5}O_2$ at 85 ºC [171].

CeO_2–Al_2O_3

Ceria has a high oxygen storage capacity and well-known catalytic and redox properties (couples of Ce^{4+}/Ce^{3+}), making more oxygen available for the oxidation process [172]. The most important property is the oxygen storage and releasing capacity of CeO_2 [173-176]. It improves CO oxidation and NO_x reduction. As is also well known, CeO_2 is a promoter additive [177-179]. Ceria-based mixed oxides such as CeO_2–MnO_x, CeO_2–Al_2O_3, CeO_2–ZrO_2, etc. have been studied intensively as catalysts for exhaust gas treatment [180-186].

The catalytic oxidation of carbon monoxide over nanostructured CeO_2–Al_2O_3 mixed oxide powders prepared by gel combustion method, using polyvinylalcohol and metal nitrates as starting materials, was studied in [187]. The dependence of CO conversion efficiency on Ce/Al molar ratio was also studied. The results showed that the bee's nest-like nanostructure with the pore wall consisting of CeO_2–Al_2O_3 mixed oxide nanocrystals was observed for samples calcined at temperatures in the range of 600–850 ºC. For the optimized sample with this nanostructure, an average grain size of 10 nm, an average pore size of 300 nm, a specific surface area of 87.5 m^2/g, and a CO conversion efficiency as high as 99.7% at 160 ºC were obtained.

Conclusions

The development of active and stable catalysts without noble metals for low-temperature CO oxidation at low temperatures is a significant challenge. Active nanocatalysts developed on the basis of nobel metals completely convert CO at temperatures even at below 0 ºC. Au/carrier catalysts have similar results, even with 1-2% of Au concentration, which significantly reduces the cost of catalysts. On non-noble catalysts complete CO oxidation obtained on $Mn_{0.5}Ce_{0.5}O_2$ at 77 ºC, Co_3O_4 nanorods can be steadily active for CO oxidation at a temperature as low as –77 ºC. The high activity of Co_3O_4 on CO oxidation is likely to be due to the relatively low ΔH of vaporization of O_2. This means that the Co–O bond strength of Co_3O_4 is relatively weak, so easily reactive oxygen can be obtained from the lattice oxygen. High activity of catalysts at low temperatures was connected with nanosize particles and high surface area. The Co-precipitation method is considered to be prospective for industrial applications, but it is still a time consuming, multi-stage method. In this respect, solution combustion synthesis has definitely advantages by comparison to the method, because of the very short time of preparation and simplicity. It can be proposed to investigate unsupported as well as supported $CuCr_2O_4$-CeO_2 nano-sized catalysts for future applications of CO oxidation.

This review summarize main directions of catalyst improvement and can be helpful for challenging development of new low temperature nanocatalysts for CO oxidation.

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References

[1]. A.A. Gokhale, J.A. Dumesic, M.J. Mavrikakis, Am. Chem. Soc. 130 (2008) 1402−1414.

[2]. L.L. Wang, L.M. Yang, Y.H. Zhang, W. Ding, S.P. Chen, W.P. Fang, Y.Q. Yang, Fuel Process. Technol. 91 (2010) 723−728.

[3]. M. Shelef, and R.W. McCabe, Catal. Today 62 (2000) 35−50.

[4]. G. Lenaers, Sci. Total Environ. 189–190 (1996) 139−147.

[5]. R.C. Rijkeboer, Catal. Today 11 (1991) 141−150.

[6]. D.L. Trimm, and Z.I. Önsan, Catal. Rev. Sci. Eng. 43 (2001) 31–84.

[7]. S.H. Oh, and G.B. Hoflund, J. Catal. 245 (2007) 35–44.

[8]. G. Xanthopoulou, Appl. Catal. A: Gen. 182 (2) (1999) 285−295.

[9]. G. Xanthopoulou, Appl. Catal. A: Gen.187 (1) (1999) 79−88.

[10]. G. Xanthopoulou, Chem. Eng. Technol. 24 (10) (2001) 1025−1034.

[11]. G. Xanthopoulou, Appl. Catal. A: Gen. 185 (1999) 185−192.

[12]. G. Xanthopoulou, Appl. Catal. B: Environ. 19 (1998) 37−44.

[13]. G. Xanthopoulou, G.A. Vekinis, Eurasian Chemico-Technological Journal 12 (1) (2010) 17−21.

[14]. P. Bera, K.C. Patil, V. Jayaram, G.N. Subbanna, M.S. Hegde, J. Catal. 196 (2) (2000), 293–301.

[15]. G. Xanthopoulou, S. Varitis, K. Karanasios, G. Vekinis, SHS Journal 23 (2) (2014) 92−100.

[16]. K. Karanasios, G. Xanthopoulou, G. Vekinis, L. Zoumpoulakis, Int. J. Self-Propag. High-Temp Synth. 23 (4) (2014) 221−231.

[17]. M. Piumetti, D. Fino, N. Russo, Appl. Catal. B: Environ. 163 (2015) 277–287.

[18]. C.-F. Yan, H. Chen, R.-R. Hu, S. Huang, W. Luo, C. Guo, M. Li, W. Li, Int. J. Hydrogen Energy 39 (32) (2014) 18695–18701.

[19]. L.H. Reddy, G.K. Reddy, D. Devaiah, B.M. Reddy, Appl. Catal. A: Gen. 445–446 (2012) 297–305.

[20]. G. Sedmak, S. Hocevar, J. Levec, J. Catal. 135 (2003) 135−150.

[21]. J.B. Wang, D.H. Tsai, T.J. Huang, J. Catal. 208 (2002) 370−380.

[22]. J.L. Ayastuy, A. Gurbani, M.P. González, Marcos, M. A. Gutiérrez, Ortiz, Ind. Eng. Chem. Res. 48 (2009) 5633−5641.

[23]. H.L. Zhang, L.H. Ren, A.H. Lu, W.C. Li, Chin. J. Catal. 33 (2012) 1125−1132.

[24]. P. Bera, K.C. Patil, V. Jayaram, G.N. Subbanna, M.S. Hegde J. Catal. 196 (2000) 293–301.

[25]. E.M. Slavinskaya, R.V. Gulyaev, A.V. Zadesenets, O.A. Stonkus, V.I. Zaikovskii, Yu. V. Shubin, S.V. Korenev, A.I. Boronin, Appl. Catal. B: Environ. 166–167 (2015) 91–103.

[26]. J. L.Margitfalvi, I. Borbáth, M. Hegedűs, Á. Szegedi, K. Lázár, S. Gőbölös, S. Kristyán, Catal. Today 73 (2002) 343–353.

[27]. A. Biabani, M. Rezaei, Z. Fattah, J. Nat. Gas Chem. 21 (2012) 415–420.

[28]. D.S. Afanasev, O.A. Yakovina, N.I. Kuznetsova, A.S. Lisitsyn, Catal. Commun. 22 (2012) 43–47.

[29]. A. Sandoval, A. Aguilar, C. Louis, A. Traverse, R. Zanella, J. Catal. 281 (2011) 40–49.

[30]. X. Zhang, Zh. Qu, X. Li, M. Wen, X. Quan, D. Ma, J. Wu, Sep. Purif. Technol. 72 (2010) 395–400.

[31]. A. Biabani-Ravandi, M. Rezaei, Z. Fattah, Chem. Eng. J. 219 (2013) 124–130.

[32]. S.H. Taylor, C. Rhodes, Catal. Today 114 (2006) 357–361.

[33]. M. Haruta, T. Kobayashi, H. Sano, N. Yamada, Chem. Lett. 16 (1987) 405–408.

[34]. M. Haruta, Stud. Surf. Sci. Catal. 110 (1997) 123–134.

[35]. M. Date, M. Okumura, S. Tsubota, M. Haruta, Angew. Chem. Int. Edn Engl. 43 (2004) 2129–2132.

[36]. M. Haruta, S. Tsubota, T. Kobayashi, H. Kageyama, M.G. Genet, B. Delmon, J. Catal. 144 (1) (1993) 175–192.

[37]. H.Y. Kim, H.M. Lee, G. Henkelman, J. Am. Chem. Soc. 134 (2012) 1560−1570.

[38]. M. Haruta, M. Date, Appl. Catal. A: Gen. 222 (2001) 427–437.

[39]. M. Haruta, Catal. Today 36 (1997) 153–156.

[40]. M.R. Benjaram, T. Gode, L. Katta. Chin. J. Catal. 32 (2011) 800–806.

[41]. Q.L. Li, Y.H. Zhang, G.X. Chen, J.Q. Fan, H. Q. Lan, Y.Q. Yang, J. Catal. 273 (2010) 167–176.

[42]. I. Dobrosz-Gómez, I. Kocemba, J.M. Rynkowski, Appl. Catal. B 83 (2008) 240–255.

[43]. H. Masatake, Catalysis Surveys of Japan 1 (1997) 61–73.

[44]. M. Haruta, N. Yamada, T. Kobayashi, S. Iijima, J. Catal. 115 (1989) 301–309.
[45]. H. Falsig, B. Hvolbaek, I.S. Kristensen, T. Jiang, T. Bligaard, C.H. Christensen, J.K. Norskov, Angew. Chem., Int. Ed. 47 (2008) 4835–4839.
[46]. H. Hakkinen, W. Abbet, A. Sanchez, U. Heiz, U. Landman, Angew. Chem., Int. Ed. 42 (2003) 1297–1300.
[47]. A. Roldan, S. Gonzalez, J.M. Ricart, F. Illas, ChemPhysChem. 10 (2009) 348–351.
[48]. B. Yoon, P. Koskinen, B. Huber, O. Kostko, B. von Issendorff, H. Hakkinen, M. Moseler, U. Landman, ChemPhysChem 8 (2007) 157–161.
[49]. N. Lopez, J.K. Norskov, J. Am. Chem. Soc. 124 (2002) 11262–11263.
[50]. I.N. Remediakis, N. Lopez, J.K. Norskov, Angew. Chem., Int. Ed. 44 (2005) 1824–1826.
[51]. B. Yoon, H. Hakkinen, U. Landman, A.S. Worz, J.M. Antonietti, S. Abbet, K. Judai, U. Heiz, Science 307 (2005) 403–407.
[52]. Z.P. Liu, X.Q. Gong, J. Kohanoff, C. Sanchez, P. Hu, Phys. Rev. Lett. 91: 266102 (2003).
[53]. L.M. Molina, B. Hammer, J. Chem. Phys. 123: 161104 (2005).
[54]. L.M. Molina, M.D. Rasmussen, B. Hammer, J. Chem. Phys. 120: 7673 (2004).
[55]. J.A. Rodriguez, J. Evans, J. Graciani, J.B. Park, P. Liu, J. Hrbek, J.F. Sanz, J. Phys. Chem. 113: 7364 (2009).
[56]. S. Tsubota, D.A.H. Cunningham, Y. Bando and M. Haruta, Preparation of Catalysts VI, Elsevier, Amsterdam, 1995, pp. 227–235.
[57]. G.C. Bond, D.T. Thompson, Gold Bull. 33 (2000) 41–50.
[58]. M. Haruta, CATTECH 6 (2002) 102–115.
[59]. M. Haruta, S. Tsubota, in: A. Wieckowski, E.R. Savinova, C.G. Constantinos (Eds.), Catalysis and Electrocatalysis at Nanoparticle Surface, Marcel Dekker, New York, 2003, p. 645.
[60]. M.M. Schubert, S. Hackenberg, A.C. van Veen, M. Muhler, V. Plzak, R.J. Behm, J. Catal. 197 (2001) 113–122.
[61]. A.I. Kozlov, A.P. Kozlova, H. Liu, Y. Iwasawa, Appl. Catal. A: Gen. 182 (1999) 9–28.
[62]. M. Okumura, S. Tsubota, M. Haruta, J. Mol. Catal. A: Chem. 199 (1-2) (2003) 73–84.
[63]. Z.P. Hao, L. An, H. Wang, Sci. Chin. (Ser. B) 44 (2001) 596–605.
[64]. B.L. Moroz, P.A. Pyrjaev, V.I. Zaikovskii, V.I. Bukhtiyarov, Catal. Today 144 (2009) 292–305.
[65]. D. Wang, Z. Hao, D. Cheng, X. Shi, C. Hu, J. Mol. Catal. A: Chem. 200 (2003) 229–238.
[66]. F. Boccuzzi, A. Chlorino, S. Tsubota, M. Haruta, J. Phys. Chem. 100 (1996) 3625–3631.
[67]. B. Nkosi, N.J. Coville, G.J. Hutchings, M.D. Adams, J. Friedl, F.E. Wagner, J. Catal. 128 (1991) 366–377.
[68]. N.A. Hodge, C.J. Kiely, R. Whyman, M.R.H. Siddiqui, G.J. Hutchings, Q.A. Pankhurst, F.E. Wagner, R.R. Rajaram, S.E. Golunski, Catal. Today 72 (2002) 133–144.
[69]. G.J. Hutchings, M.S. Hall, A.F. Carley, P. Landon, B.E. Solsona, C.J. Kiely, A. Herzing, M. Makkee, J.A. Moulijn, A. Overweg, J.C. Fierro-Gonzalez, J. Guzamn, B.C. Gates, J. Catal. 242 (2006) 71–81.
[70]. M. Khoudiakov, M.C. Gupta, S. Deevi, Nanotechnology 15 (2004) 987.
[71]. G.J. Hutchings, Catal. Today 100 (2005) 55–61.
[72]. S. Al-Sayari, A.F. Carley, S.H. Taylor, G.J. Hutchings, Top. Catal. 44 (2007) 123–128.
[73]. M. Khoudiakov, M.C. Gupta, S. Deevi, Appl. Catal. A 291 (2005) 151–161.
[74]. P. Landon, J. Ferguson, B.E. Solsona, T. Garcia, A.F. Carley, A.A. Herzing, C.J. Kiely, S.E. Golunski, G.J. Hutchings, Chem. Commun. 27 (2005) 3385–3387.
[75]. L. Ruihui, Z. Cunman, M. Jianxin, Journal Of Rare Earths 28 (3) (2010) 376–382.
[76]. E. Auer, A. Freund, J. Pietsch, T. Tacke, Appl. Catal. A 173 (1998) 259–271.
[77]. C. Bianchi, F. Porta, L. Prati, M. Rossi, Top. Catal. 13 (2000) 231–236.
[78]. L. Prati, G. Martra, Gold Bull. 32 (1999) 96–101.
[79]. D.A. Bulushev, I. Yuranov, E.I. Suvorova, P.A. Buffat, and L. Kiwi-Minsker, J. Catal. 224 (2004) 8–17.
[80]. S. Carrettin, P. Concepcio´ n, A. Corma, J.M. Lo´ pez Nieto, V.F. Puntes, Angew. Chem. Int. Ed. 43 (2004) 2538–2540.
[81]. N. Russo, D. Fino, G. Saracco, V. Specchia, Catal. Today 117 (2006) 214–219.
[82]. F. Arena, P. Famulari, G. Trunfio, G. Bonura, F. Frusteri, L. Spadaro, Appl. Catal. B: Environ. 66 (2006) 81–91.
[83]. L.F. Liotta, G. Di Carlo, A. Longo, G. Pantaleo, A.M. Venezia, Catal. Today 139 (2008) 174–179.
[84]. U.R. Pillai, S. Deevi, Appl. Catal. A: Gen. 299 (2006) 266–273.
[85]. L.-H. Chang, N. Sasirekha, B. Rajesh, Y.-W. Chen, Sep. Purif. Technol. 58 (2007) 211–218.
[86]. A. Wolf, F. Schuth, Appl. Catal. A: Gen. 226 (2002) 1–13.
[87]. P. Konova, A. Naydenov, T. Tabakova, D. Mehandjiev, Catal. Commun. 5 (2004) 537–542.
[88]. X. Zhang, H. Wang, B.-Q. Xu, J. Phys. Chem. B 109 (2005) 9678–9683.
[89]. S.-P. Wang, T.-Y. Zhang, X.-Y. Wang, S.-M. Zhang, S.-R. Wang, W.-P. Huang, S.-H. Wu, J. Mol. Catal. A: Chem. 272 (2007) 45–52.
[90]. I. Dobrosz-Go´mez, I. Kocemba, J.M. Rynkowski, Appl. Catal. B: Environ. 88 (2009) 83–97.

[91]. T.-J. Huang, D.-H. Tsai, Catal. Lett. 87 (2003) 173–178.
[92]. T.-J. Huang, T.-C. Yu, Appl. Catal. 71 (2) (1991) 275–282.
[93]. J.T. Kummer, Prog. Energy Combust. Sci. 6 (1980) 177–199.
[94]. B. Skarman, T. Nakayama, D. Grandjean, R.E. Benfield, E. Olsson, K. Niihara, L.R. Wallenberg, Chem. Mater. 14 (2002) 3686–3699.
[95]. B. Skarman, D. Grandjean, R. E. Benfield, A. Hinz, A. Anderson, L.R. Wallenberg, J. Catal. 211 (2002) 119–133.
[96]. W. Liu, M.F. Stephanopoulos, Chem. Eng. J. 64 (2) (1996) 283–294.
[97]. A. Tschope, J.Y. Ying, Y.-M. Chiang, Mater. Sci. Eng. A 204 (1995) 267–271.
[98]. G. Avgouropoulos, T. Ioannides, Appl. Catal. A: Gen. 244 (2003) 155–167.
[99]. L.K. Kundakovic, M.F. Stephanopoulos, Appl. Catal. A: Gen. 171 (1998) 13–29.
[100]. R. Bechara, G. Wrobel, C.F. Aissi, M. Guelton, J.P. Bonnelle, A. Abou-Kais, Chem. Mater. 2 (1990) 518–522.
[101]. X.-Y. Jiang, R.-X. Zhou, P. Pan, B. Zhu, X.-X. Yuan, X.-M. Zheng, Appl. Catal. A: Gen. 150 (1997) 131–141.
[102]. U.R. Pillai, S. Deevi, Appl. Catal. B: Environ. 64 (2006) 146–151.
[103]. F.C. Buciuman, F. Patcas, T. Hahn, Chem. Eng. Process. 38 (1999) 563–569.
[104]. D.M. Whittle, A.A. Mirzaei, J.S.J. Hargreaves, R.W. Joyner, C.J. Kiely, S.H. Taylor, G.J. Hutchings, Phys. Chem. 4 (2002) 5915–5920.
[105]. S.H. Taylor, G.J. Hutchings, A.A. Mirzaei, Chem. Commun. (1999) 1373–1374.
[106]. J. Agrell, M. Boutonnet, I. Melia´n-Cabrera, J.L.G. Fierro, Appl. Catal. A: Gen. 253 (2003) 201–211.
[107]. X. Xi, S. Ma, J.-F. Chen, Y. Zhang, J. Environmental Chem. Engineering 2 (2014) 1011–1017.
[108]. D.R. Merrill, C.C. Scalione, J. Am. Chem. Soc. 43 (1921) 1982–2002.
[109]. C. Yoon, D.L. Cocke, J. Catal. 113 (1988) 267–280.
[110]. A.A. Mirzaei, H.R. Shaterian, R.W. Joyner, M. Stockenhuber, S.H. Taylor, G.J. Hutchings, Catal. Commun. 4 (2003) 17–20.
[111]. A.A. Mirzaei, H.R. Shaterian, M. Kaykhaii, Appl. Surf. Sci. 239 (2005) 246–254.
[112]. C. Jonesa, K.J. Colea, S.H. Taylor, M.J. Crudaceb, G.J. Hutchings,J. Mol. Catal. A: Chem. 305 (2009) 121–124.
[113]. M. Li, D.-H. Wang, X.-C. Shi, Z.-T. Zhang, T.-X. Dong, Sep. Purif. Technol. 57 (2007) 147–151.
[114]. T. Cheng, Z.Y. Fang, Q.X. Hu, K.D. Han, X.Z. Yang, Y.J. Zhang, Catal. Commun. 8 (2007) 1167–1171.
[115]. H.G. El-Shobaky, M.M. Mokhtar, Appl. Surf. Sci. 253 (2007) 9407–9413.
[116]. H.G. El-Shobaky, Y.M. Fahmy, Mater. Res. Bull. 41 (2006) 1701–1713.
[117]. W.M. Shaheena, A.A. Ali, Int. J. Inorg. Mater. 3 (2001) 1073–1081.
[118]. E. Boellaard, F.Th. van de Scheur, A.M. van de Kraan, J.W. Geus, Appl. Catal. A: Gen. 171 (1998) 333–350.
[119]. J.-L. Cao, Y. Wang, X.-L. Yu, S.-R. Wang, S.-H. Wu, Z.-Y. Yuan, Appl. Catal. B: Environ. 79 (2008) 26–34.
[120]. S.H. Taylor, G.J. Hutchings, A.A. Mirzaei, Catal. Today 84 (2003) 113–119.
[121]. U.R. Pillai, S. Deevi, Appl. Catal. B: Environ. 65 (2006) 110–117
[122]. G. Marbán, A.B. Fuertes, Appl. Catal. B: Environ. 57 (2005) 43–53
[123]. D.H. Kim, J.E. Cha, Catal. Lett. 86 (2003) 107–112.
[124]. X.L. Tang, B.C. Zhang, Y. Li, Y.D. Xu, Q. Xin, W.J. Shen, Catal. Today, 93–95 (2004) 191–198.
[125]. M.-F. Luo, X.-X. Yuan, X.-M. Zheng, Y.-J. Zhong, Appl. Catal. A: Gen.162(1997) 121–131.
[126]. W. Liu, M. Flytzani-Stephanopoulos, J. Catal. 153 (1995) 304–316.
[127]. Y. Liu, H.-L. Sun, Q.-S. Liu, H.-F. Jin, Chin. J. Catal. 22 (2001) 453–456.
[128]. P.G. Harrison, I.K. Ball, W. Azelee, W. Daniell, D. Goldfarb, Chem. Mater. 12 (2000) 3715–3725.
[129]. S. Bjorn, G. Didier, E.B. Robert, H. Andreas, A. Arne, L.R. Wallenberg, J. Catal. 211 (2002) 119–133.
[130]. G. Avgouropoulos, T. Ioannides, C. Papadopoulou, J. Batista, S. Hocevar, H.K. Matralis, Catal. Today 75 (2002) 157–167.
[131]. T. Hu, J. Yang, J. Zhao, D. Wang, H. Song, L. Chou, Chin. J. Catal. 28 (10) (2007) 844–846.
[132]. X.-C. Zheng, S.-H. Wu, S.-P. Wang, S.-R. Wang, S.-M. Zhang, W.-P. Huang, Appl. Catal. A: Gen. 283 (2005) 217–223.
[133]. Z.-Q. Zou, M. Meng, L.-H. Guo, Y.-Q. Zha, J. Hazard. Mater.163 (2009) 835–842.
[134]. G. Chen, Q. Li, Y. Wei, W. Fang, Y. Yang, Chin. J. Catal. 34 (2013) 322–329.
[135]. J. Jansson, J. Catal. 194 (2000) 55–60.
[136]. J. Jansson, A.E.C. Palmqvist, E. Fridell, M. Skoglundh, L.O. Sterlund, P. Thormahlen, V. Langer, J. Catal. 211 (2002) 387–397.
[137]. H.K. Lin, C.B. Wang, H.C. Chiu, S.H. Chien, Catal. Lett. 86 (2003) 63–68.
[138]. H.K. Lin, H.C. Chiu, H.C. Tsai, S.H. Chien, C.B. Wang, Catal. Lett. 88 (2003) 169–174.
[139]. C.B. Wang, C.W. Tang, S.J. Gau, S.H. Chien,

Catal. Lett. 101 (2005) 59–63.
[140]. P. Broqvist, I. Panas, H. Person, J. Catal. 210 (2002) 198–206.
[141]. B.A. Sazonov, V.V. Popovskii, G.K. Boreskov, Kinet. Catal. 9 (1968) 255.
[142]. M. Haneda, Y. Kintaichi, N. Bion, H. Hamada, Appl. Catal. B: Environ. 46 (2003) 473–482.
[143]. D.S. Lafyatis, G.P. Ansell, S.C. Bennett, J.C. Frost, P.J. Millington, R.R. Rajaram, A.P. Walker, T.H. Ballinger, Appl. Catal. B: Environ. 18 (1998) 123–125.
[144]. Y.Y. Yao, J. Catal. 33 (1974) 108–122.
[145]. D. Perti, R. L. Kabel, AIChE J. 31 (1985) 1420–1440.
[146]. D.A.H. Cunningham, T. Kobayashi, N. Kamijo, M. Haruta, Catal. Lett. 25 (1994) 257–264.
[147]. F. Grillo, M.M. Natile, A. Glisenti, Appl. Catal. B: Environ. 48 (2004) 267–274.
[148]. X. Xie, Y. Li, Z.-Q. Liu, M. Haruta, W. Shen, Nature 458 (2009) 746–749.
[149]. C. Liu, Q. Liu, L. Bai, A. Dong, G. Liu, S. Wen, J. Mol. Catal. A: Chem. 370 (2013) 1–6.
[150]. M.J. Pollard, B.A. Weinstock, T.E. Bitterwolf, P.R. Griffiths, A.P. Newbery, J.B. Paine, J. Catal. 254 (2008) 218–225.
[151]. P. Thormählen, M. Skoglundh, E. Fridell, B. Andersson, J. Catal. 188 (1999) 300–310.
[152]. C.-W. Tang, C.-C. Kuo, M.-C. Kuo,C.-B.Wang, S.-H. Chien, Appl. Catal. A: Gen. 309 (2006) 37–43.
[153]. J.C.W. Frazer, C.G. Albert, J. Phys. Chem. 40 (1936) 101–112.
[154]. M. Shelef, K. Otto, H. Gandhi, J. Catal. 12 (1968) 361–375.
[155]. C.A. Leech, L.E. Campbell, Adv. Chem. Ser. 143 (1975) 161–171.
[156]. S.A. Solovev, S.N. Orlik, Kinet. Catal. 50 (5) (2009) 705–714.
[157]. S. Stegenga, R.van Soest, F. Kapteijn, J.A. Moulijn, Appl. Catal. B: Environ. 2 (1993) 257–275.
[158]. K.S.R.C. Murthy, J. Ghose, J. Catal. 147 (1994): 171–176.
[159]. R. Prasad, P. Singh, Cat. Rev. - Sci. Eng. 54 (2) (2012) 224–279.
[160]. G. Xanthopoulou, G. Vekinis, Adv. Environ. Res. 5 (2001)117–128.
[161]. H.I. Hsiang, F.S. Yen, Ceram. Int, 29 (1) (2003) 1-6.
[162]. E. Manova, D. Paneva, B. Kunev, C. Estournes, E. Riviere, K. Tenchev, A. L´eaustic, I. Mitov. J. Alloy Compd. 485 (2009) 356–361.
[163]. V. Pillai, D.O. Shah. J. Magn. Magn. Mater. 163 (1996) 243–248.
[164]. N. Moumen, M. P. Pileni, Chem. Mater. 8 (1996) 1128–1134.
[165]. J.J. Melchiore US Patent 3 055 839. 1962.
[166]. F. Bensebaa, F. Zavaliche, P. L'Ecuyer, R. W. Cochrane, T. Veres, J. Colloid. Interface Sci. 277 (2004) 104–110.
[167]. L.J. Cote, A.S. Teja, A.P. Wilkinson, Z.J. Zhang. Fluid Phase Equilib. 210 (2003) 307–317.
[168]. T. Meron, Y. Rosenberg, Y. Lereah, G. Markovich J. Magn. Magn. Mater. 292 (2005) 11–16.
[169]. Y.I.D. Kim, C.S. Lee, Physica B 337 (2003) 42–51.
[170]. A. Biabani-Ravandi, M. Rezaei, Chem. Eng. J., 184 (1) (2012) 141–146.
[171]. E.Yu. Liberman, B.S. Kleusov, A.I. Mihailichenko, T.V. Konkova, A.V. Horoshilov, Kataliz v promyshlennosti [Catalysis in the industry] 3 (2012) 44–49 (in Russian).
[172]. A. Martinez-Arias, M. Fernandez-Garcia, O. Galvez, J.M. Coronado, J.A. Anderson, J.C. Conesa, J. Soria, G. Munuera, J. Catal. 195 (2000) 207–216.
[173]. A. Martinez-Arias, R. Cataluna, J.C. Conesa, J. Soria, J. Phys. Chem. B 102 (1998) 809–817.
[174]. C. Serre, F. Garin, G. Belot, G. Maire, J. Catal. 141 (1993) 1–9.
[175]. S.H. Oh, J. Catal. 124 (1990) 477–487.
[176]. H.C. Yao, Y.F.Y. Yao, J. Catal. 86 (1984) 254–265.
[177]. C.W. Tang, C.C. Kuo, M.C. Kuo, C.B. Wang, S.H. Chien, Appl. Catal. A: Gen. 309 (1) (2006) 37–43.
[178]. A. Trovarelli, Catal. Rev. Sci. Eng. 38 (1996) 439–520.
[179]. J.C. Summers, S.A. Ausen, J. Catal. 58 (1979) 131–143.
[180]. K. Tikhomirov, O. Krocher, M. Elsener, A. Wokaun, Appl. Catal. B: Environ. 64 (2006) 72–78.
[181]. X. Liu, J. Lu, K. Qian, W. Huang, M. Luo, J. Rare Earths 27 (2009) 418–424.
[182]. X. Wu, S. Liu, D. Weng, F. Lin, Catal. Commun. 12 (2011) 345–348.
[183]. S. Bose, Y. Wu, J. Am. Ceram. Soc. 88 (2005) 1999–2002.
[184]. A. Martı´nez-Arias, M. Ferna´ndez-Garcı´a, L.N. Salamanca, R.X. Valenzuela, J.C. Conesa, J. Soria, J. Phys. Chem. B 104 (2000) 4038–4046.
[185]. K.M.S. Khalil, J. Colloid Interface Sci. 307 (2007) 172–180.
[186]. D. Terribile, A. Trovarelli, J. Llorca, C. deLeitenburg, G. Dolcetti, Catal. Today 43 (1998) 79–88.
[187]. D.N. Nhiema, L.M. Daia, N.D. Van, D.T. Lim, Ceram. Int. 39 (2013) 3381–3385.

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