DEEP AND SELECTIVE CO OXIDATION ON NANOCRYSTALLINE CERIA SUPPORTED CATALYSTS

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Carbon monoxide is one of the most important toxic gaseous pollutants. Current legislation requires very low CO emissions, which could not be achieved only with the modification of fuel burning processes. From the other side polymeric materials used in modern fuel calls elements construction have very high sensitivity to CO, even 20 ppm of carbon monoxide in the stream can irreversibly destroy them. A large number of catalysts were tested in this reaction, but the further developments in achieving 100% CO conversion at close to room temperatures on non-precious metal catalysts are still needed. At present time ceria is one of the most promising catalytic supports which can activate and accumulate oxygen during catalytic reactions.

Ceria was synthesized from $Ce(NO_3)_3$ solution in *iso*-propanol-water mixture(1:3) using ammonia as a reducing agent. After filtering and drying procedures obtained sample was calcined at 400 ^{O}C. Using BET, XRD and TEM it was shown that surface area of CeO_2 is 120 m^2/g, the average pore diameter is 1.8 nm and the average particle size is near 5 nm with near uniform particle size distribution. The catalysts were prepared by incipient wetness method from corresponding metal nitrates solution, except $5\%Ni_S$ catalyst which was prepared from Ni sulfate. All samples was dried at 95 ^{O}C for 5 h, then they where calcined in air flow in temperature programmed regime from 100→400 ^{O}C for 2 hours.CO oxidation reaction was performed on all catalysts in fixed-bed reactors using 2 different gaseous mixtures - $4\%CO/2{,}05\%O_2$ in He (with GC as analyzer) and $0{,}2\%CO/8\%O_2$ in N_2 mixture (with electrochemical CO detector) and the same WHSV = 10,000 h^{-1}.

Table 1. Deep CO conversion parameters on nanocrystalline ceria based catalysts.

Catalyst	4% CO / 2.05% O+ in He		2000 ppm CO / 8% O_2 in N_2	
	T50% conv., ^{O}C	T 99,5% conv., ^{O}C	T 50% conv., ^{O}C	T CO<20ppm, ^{O}C
CeO_2	320	400	300	not achieved
5%Cu/CeO_2	45	67	25	130
5%Co/CeO_2	125	180	70	260
5%Fe/CeO_2	180	275	160	375
5%NiMg/CeO_2	175	285	170	305
5%Ni_S/CeO_2	290	410	110	not achieved
5%Ni/CeO_2	125	160	115	220

It was shown that addition of any metallic component leads to decrease of 50% and 99% CO conversion temperatures comparing to pure CeO_2. The most active copper sample can convert CO even at room temperature (near 25% of overall CO), moreover, its 100% activity remains unchanged in the wide range of temperatures 100-400 ^{O}C therefore it can be good candidate for process of selective CO removal from hydrogen containing streams for fuel cells purposes.

The further tests of the set of 1-30%Cu/CeO_2 catalysts in selective CO oxidation (gas composition – 2.1%O_2/0.9%CO/40%H_2/He, WHSV = 10000 h^{-1}) have shown that all of the catalysts can remove CO at temperatures between 90-300 ^{O}C, but at high temperatures 140-300 ^{O}C water formation also proceeds. The optimal copper loadings were found between 3-10%. Further increase of copper loading promotes blockage of ceria particles by copper which leads to decrease of activity.

Thus the ceria supported catalysts was found to be active in deep and selective CO oxidation reaction. High close to room temperature activity make them very attractive for the use in home CO neutralizers which can be placed near possible CO sources like domestic ovens or air heaters.