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Alkali resistivity of Cu based selective catalytic reduction catalysts: Potassium chloride aerosol exposure and activity measurements

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Abstract

The deactivation of $V_2O_5-WO_3-TiO_2$, Cu-HZSM5 and Cu-HMOR plate type monolithic catalysts was investigated when exposed to KCl aerosols in a bench-scale reactor. Fresh and exposed catalysts were characterized by selective catalytic reduction (SCR) activity measurements, scanning electron microscope-energy dispersive X-ray spectroscopy (SEM-EDX) and NH_3 -temperature programmed desorption (NH_3 -TPD). 95% deactivation was observed for the $V_2O_5-WO_3-TiO_2$ catalyst, while the Cu-HZSM5 and Cu-HMOR catalysts deactivated of only 58% and 48%, respectively, after 1200 h KCl exposure. SEM analysis of the KCl aerosol exposed catalysts revealed that the potassium salt not only deposited on the catalyst surface, but also penetrated into the catalyst wall. Thus, the K/M ratio (M = V or Cu) was high on $V_2O_5-WO_3-TiO_2$ catalyst and comparatively less on Cu-HZSM5 and Cu-HMOR catalysts. NH_3 -TPD revealed that the KCl exposed Cu-HZSM5 and Cu-HMOR catalysts only experienced a slight loss of acidity while the $V_2O_5-WO_3-TiO_2$ catalyst lost most of the acidity. High alkali resistivity seems to be characteristic of the zeolite supported SCR catalysts which thus could be attractive for flue gas cleaning in biomass plants.

Keywords: SCR of NO with NH_3 ; Cu-zeolite catalysts; Biomass fired power plants

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1. Introduction

The selective catalytic reduction (SCR) of nitrogen oxides (NO_x) with NH_3 as the reducing agent has been recognised as the most effective method for removal of NO_x from stationary sources of energy by combustion of fossil fuels [1-4]. The catalyst consists of V_2O_5 dispersed on the surface of a TiO_2 carrier. In order to enhance activity and robustness of the catalyst other metal oxides are added as promoters, mostly WO_3 or MoO_3 . The NH_3 -SCR process is furthermore considered to have the highest potential to meet strict diesel emission standards in mobile applications [5, 6].

In principle a SCR catalyst should be durable, since it is not consumed during the reaction. This is unfortunately not the case, since it deactivates over time. Catalyst deactivation can be categorized in two types: physical and chemical deactivation. Physical deactivation occurs when the pores or channels in the catalyst structure clogs, resulting in a diminishing of the surface area and the number of accessible active surface sites. This can be caused either by dust in the off-gas or by deposition of salts formed during the combustion. Chemical deactivation occurs when a compound reacts with an active site, and thereby makes the site catalytically inactive.

Biomass includes organic matter like trees, agricultural crop and timber waste, aquatic plants, animal waste, municipal and industrial waste. Contrary to fossil fuels they are regarded as environmentally sustainable energy sources, since they are part of the carbon eco-cycle on earth and thus an energy source with zero- or at least “low” CO_2 footprint. Combustion of natural gas and fossil fuels such as coal leads to a relatively clean flue gas, whereas combustion of, e.g. municipal waste or biomass, often contain species that can lead to deactivation of the traditional vanadia-titania-based SCR catalyst [7-17]. Biomass combustion result in formation of particulates with high concentration in the submicrometer range. The flue gas particles are formed via condensation,

nucleation, and chemical surface reactions of inorganic compound vapours when the gases are cooled downstream the boiler [8, 9].

The deactivation of SCR catalysts under biomass combustion has been ascribed to the potassium presence of submicrometer particles which can poison the catalyst active sites or mask them through pore fouling [7]. The element composition of various fuels and ash formed in industrial biomass fired power plants, have recently been reported [8-11]. Studies show a significant increase in the quantity of alkali and alkaline-earth elements (K, Na, Mg, Ca), phosphorous and chlorine in the flue gas produced from biomass-based fuels compared to coal [9]. The content of potassium and chlorine in straw can be more than an order of magnitude higher than in coal. Especially the high content of potassium in e.g. wood and straw, is of concern. Alkali metals were identified early as poisons for vanadia-titania based SCR catalysts by Chen and Yang [10]. They found that the strength of the poison is related to the increase in basicity of the alkali salt. Potassium salts are thus considered a stronger poison to the vanadium-based catalyst than sodium and lithium salts.

Chemical deactivation of catalysts by deposition of alkali poisons have been investigated with different methods, such as wet-chemical impregnation [5, 10-12], aerosol exposure [13] and flue gas exposure in power plants [8, 14]. Usually the wet-chemical impregnation method is preferred to screen the catalysts, since it is fast and allows the poison level of deactivation to be controlled by the amount of poison added. However, compared to lab scale wet-chemical impregnation, potassium aerosol exposure and flue gas exposure in power plants are considered as more realistic test methods.

Moradi et al. [15] found that aerosol deposition on the catalyst surface can slow down the reagent species diffusion and thereby decrease the reaction activity. Moreover, the authors reported that inorganic submicrometer particle penetration in the pore structure depends on the nature of the

species. Alkali aerosols can not only deposit on the catalyst surface but also reach the inner parts of the monolith wall due to their high diffusion coefficient. It is reported that K/V molar ratio of 0.3 is enough to completely poison the catalyst [13, 14]. Additionally, it was reported that the observed rate of deactivation is so high that use of SCR in purely straw-fired power plants seems impractical with the present industrial V_2O_5 - WO_3 - TiO_2 catalyst.

Potential alternatives to the vanadium-based SCR systems are supported Fe and Cu oxide catalysts [4, 6, 11]. Ideally, the support should be thermally stable, have high surface area and be strongly acidic in order to attract alkali metals and thus protect the active metal sites for alkali poisoning. In our previous studies, we reported alkali resistivity of Cu/zeolite and V_2O_5 /zeolite deNOx catalysts for flue gas cleaning in biomass fired applications with wet-chemical impregnation by potassium nitrate [11, 16]. A recent report on the effect of inorganic additives on Fe-zeolite catalysts showed improved poisoning resistivity compared to the industrial V_2O_5 - WO_3 - TiO_2 catalyst [6]. Currently there is no commercial catalyst available for deNOx in flue gas from biomass units. Thus it seems interesting to test zeolite based catalysts under more realistic aerosol conditions and compare with industrial V_2O_5 - WO_3 - TiO_2 catalysts.

In this work, HZSM5 and HMOR reinforced plate type catalysts are prepared by dip-coating of the glass fiber support and subsequently impregnation by a copper nitrate solution [11]. The resulting Cu-HZSM5 and Cu-HMOR catalysts were deactivated along with a V_2O_5 - WO_3 - TiO_2 (VWT) catalyst by exposure to KCl aerosols in a bench-scale reactor for 1200 h. The SCR activities of the fresh and deactivated catalysts are compared and discussed based on characterization methods. For the actual application in the power plants the catalyst should have monolithic shape and deactivation measurements of those are necessary under realistic conditions unlike fast wet impregnation poisoning of particles [16].

2. Experimental

2.1 Cu/ zeolite plate type monolith catalyst preparation

Two glass fiber plate type monoliths (Haldor Topsøe A/S, Denmark) were used as substrates for dip coating. The fiber material consists primarily of SiO_2 but also alumina and calcium to a lesser extent. The catalysts were prepared by immersing the glass fiber plate into a zeolite suspension. Two different types of zeolites (Zeolyst International) H-Mordenite ($\text{Si}/\text{Al} = 10$ and $400 \text{ m}^2/\text{g}$) and H-ZSM5 ($\text{Si}/\text{Al} = 15$ and $500 \text{ m}^2/\text{g}$) were used. The suspension was prepared by mixing 20 wt.% zeolite and 5 wt.% colloidal silica (LUDOX[®] HS - 30, particle diameter 20–24 nm, Aldrich) with demineralized water in a wet fluid mill until a stable uniform slurry was formed. The fiber plates were immersed in the suspension for 3 min each, and excess suspension was removed by air blowing. To obtain better reinforcement of zeolite on the glass fiber plate the average particle size of the suspension should be $< 5 \mu\text{m}$. The zeolite reinforced plates were dried at 120°C for 8 h and weighed to find the gain in weight. 4 wt.% Cu-zeolite catalysts were then prepared by incipient wetness impregnation of the zeolite plates using appropriate amounts of copper nitrate (Aldrich, 99.99%) solutions as precursor. The samples were finally calcined at 500°C for 4 h at a heating rate of $2^\circ\text{C}/\text{min}$. A commercial $\text{V}_2\text{O}_5\text{-WO}_3\text{-TiO}_2$ plate type catalyst (VWT) was used for comparison. The catalyst plate contained 3 wt.% V_2O_5 and about 7 wt.% WO_3 on a fiber reinforced TiO_2 carrier. The plates had dimensions of 50 mm x 160 mm x 1.3 mm and were cut into 40 mm x 120 mm x 1.3 mm for the exposure.

The particle size of the supplied zeolites was decreased using 3-5 mm glass beads in a wet fluid mill. The milling was continued until the average particle size was reduced to about 2–4 μm . The particle sizes of the supplied powders and the milled powders were determined by the laser beam scattering technique using a Malvern Mastersizer 2000 particle size analyzer (Malvern

Instruments Ltd., Worcestershire, U.K.) equipped with a sample suspension unit and an ultrasonicator. Obscurations in the range of 10–20% were used during the measurement.

2.2 KCl aerosol exposure

To expose the two Cu/zeolite catalysts (one Cu-HMOR and one Cu-HZSM5) to alkali poisons under realistic power plant conditions the plate type catalysts were placed in the pilot plant reactor shown in Fig. 1 and exposed to well-defined aerosols of KCl. For comparison one commercial vanadium catalyst (VWT) was also exposed. Hot flue gas was produced by a 50 kW natural gas burner and a solution of the salt in distilled water (7.4 g/l KCl) (Aldrich, 98%) was prepared and mixed before being added to the system. An aerosol of the salt was then generated by injecting 440 ml/h of the solution through a fluid nozzle into the flue gas close to the burner where the temperature was 1050–1100 °C. A bayonet heat exchanger was inserted into the main duct downstream the formation of the desired aerosol particles to cool down the flue gases. In this way accelerated corrosion caused by the potassium compounds was avoided. The catalyst box contains the plate catalysts was well insulated and heated by an electrical heating wire. The exposure temperature was kept at 350 °C and the temperature difference over the cross section of the catalyst box at the catalyst inlet was within 4 °C while the temperature difference between the catalyst inlet and outlet was kept less than 5 °C. A soot blower and a steel grid were installed 20 cm and 5 cm, respectively, above the catalyst to minimize plugging problems. The soot blower consisted of a steel pipe with a diameter of 16 mm and a hole of 10 mm, a time controller and connection to compressed air at a pressure of 5 bar. Two additional soot blowers were placed just above the steel grid to blow away the particles deposited on the mesh. Soot blowing was carried out by 3–5 s of blowing with compressed air at an interval of 30 min. The total flow rate at the outlet of the burner was about 60 N m³/h and the flow rate through the catalyst was kept at 40–45 N m³/h by adjusting

the bypass valve. The experiments were conducted for 1200 h continuously. After exposure the catalyst plates were removed and immediately tested for SCR activity.

2.3 SCR activity measurements

The SCR activity measurements were performed at atmospheric pressure in a fixed-bed quartz reactor. The activity was measured on cut out samples of fresh and aerosol exposed catalyst plates ($1.7 \times 1.7 \text{ cm}^2$, 0.25 g) at a total gas flow rate of 3 L/min. The composition of the feed gas was adjusted to 400 ppm NO, 500 ppm NH₃, 5% O₂, 2.4% H₂O and balance N₂ by mixing 1% NO/N₂ ($\pm 0.1\%$ abs.), 1% NH₃/N₂ (0.005% abs.), O₂ ($\geq 99.95\%$) and balance N₂ ($\geq 99.999\%$) (Air Liquide) using mass-flow controllers. Activities of the catalysts were measured at 350 °C after attaining steady state values of temperature and conversion. Steady state conversion values of NO and NH₃ gases were measured by an online ABB NDUV gas analyser. The catalytic activity is represented as the first-order rate constant (cm³/g·s), since the SCR reaction is known to be first-order with respect to NO under super stoichiometric NH₃ conditions [17]. Assuming plug flow conditions, the first-order rate constants were obtained from the conversion of NO as:

$$k = -(F_{NO}/(m_{cat} C_{NO})) \ln (1-X) \quad (1)$$

where F_{NO} denotes the molar feed rate of NO (mol/s), m_{cat} the catalyst mass (g), C_{NO} the NO concentration (mol/cm³) in the inlet gas and X the fractional conversion of NO.

2.4 Characterization

X-Ray powder diffraction (XRPD) measurements were performed on a Huber G670 powder diffractometer using CuK_α radiation within a 2θ range of 5-80° in steps of 0.02°. The BET surface area of the supports and catalysts was determined by nitrogen physisorption measurements on 100 mg samples at liquid nitrogen temperature with a Micromeritics ASAP 2010 instrument.

The samples were heated to 200 °C for 1 h prior to the measurement. For the XRPD and BET measurements the monolith sample was crushed and sieved to get powder without glass fiber.

The adherence on the zeolite plate was determined by immersing the coated monolith samples in acetone and treating it in an ultrasonic bath (45 kHz and 100 W) for 1 h. The samples were then removed and dried at 110 °C for 2 h and weighed before and after the ultrasonic treatment to determine the loss of catalytic coating.

NH₃-TPD experiments were conducted on a Micromeritics Autochem-II instrument. In a typical TPD experiment, a sample of about 10 mm x 15 mm in size was placed in a quartz tube and pretreated in flowing He at 500°C for 2 h. Then, the temperature was lowered to 100°C and the sample was treated with anhydrous NH₃ gas (Air Liquide, 5% NH₃ in He). After NH₃ adsorption, the sample was flushed with He (50 ml/min) for 60 min at 100 °C. Finally, the TPD was carried out by heating the sample from 100 to 600°C (10 °C/min) in He flow (25 ml/min).

The distribution of potassium in the exposed catalysts was investigated at the Centre for Microstructure and Surface Analysis, Danish Technological Institute by SEM-EDX on a LEO 440 microscope. The samples were prepared using an MT-990 rotary microtome. The samples were kept dry to prevent any dissolution, recrystallization, and removal of potassium compounds. Before analysis, the samples were covered with a very thin carbon film to become conductive. To compare the different spectra and samples, both carbon and oxygen were excluded from the analysis results and the amount of other elements recalculated on a carbon and oxygen free basis.

3. Results and discussion

The stability of the suspension used for coating and the adhesion of the coating to the substrate is strongly influenced by the size of the suspended particles in the slurry. It is necessary that the particle size of the zeolite powders is reduced to values smaller than 5 µm in order to obtain

a stable coat [18, 19]. Initial particle sizes (D_{50}) of the HZSM5 and HMOR were found to be 8.3 and 13.7 μm , respectively. However, the particle size of the original samples was reduced to $< 5 \mu\text{m}$ size by milling. The size distribution of the zeolite samples after wet milling is presented in Fig. 2 and the values are reported in Table 1. The average particle size of HZSM5 was 3.6 μm and 90% of the powder particles were smaller than 8.0 μm . HMOR presented an average particle size of 3.1 μm and 90% was smaller than 17.7 μm . The particle size distribution of HZSM5 was sharp and symmetric while that of HMOR was broad and asymmetric in shape. Similar particle size distribution patterns were reported by Zamaro et al. for environmental applications of zeolite washcoating honeycomb reactors [20].

The characteristics of the coating depend on various properties of the slurry which in turn depends on the viscosity, pH, solid concentration of the slurry, and the properties of the solid particles [18-20]. Optimum conditions result in better coating which could be checked by minimum loss of weight during the adherence test. Adhesion of the coating is an important parameter to be considered for environmental applications of the catalysts which involve high flows and temperatures as well as soot blowing. Table 1 shows the weight percent of zeolite loss after the ultrasonic test. HZSM5 and HMOR coated plates showed 48 and 37 wt.% loss. The better adhesion of HMOR could be due to the smaller particle size (D_{50}) which facilitated strong anchoring on to the substrate. In the present investigation the weight loss was less compared to the reported results without the colloidal silica binder [21]. The colloidal silica has an important effect in enhancing the adhesion of the coating. The small size of the binder particles leading to the filling of the space between the carrier aggregates thus increases the bonding between particles.

In order to deactivate the monolithic catalyst plates, KCl aerosols are generated by injection of the KCl solution at the exit of the burner. Characteristics of the aerosols produced in the bench-scale reactor were reported in our previous articles [13, 14]. Addition of 7.4 g/l KCl solution (440 ml/h)

corresponds to a calculated aerosol concentration of 53 mg/(Nm³) at 1050°C. This feed allows continuous operation of the burner and aerosol exposure possible for many hours. The average aerodynamic diameter of KCl aerosols in the bench-scale reactor was about 0.3 µm which is similar to aerosols in the flue gas of Danish straw-fired grate boilers [13].

The XRPD patterns of fresh and KCl exposed catalysts are shown in Fig. 3. Fresh VWT catalyst showed only support anatase TiO₂ patterns indicating that the V₂O₅ and WO₃ are highly dispersed on the support. Fresh Cu-HZSM5 and Cu-HMOR catalysts showed only support zeolite patterns also indicating that CuO is highly dispersed in an amorphous state on the surface of the zeolite support. KCl exposed catalysts had almost similar diffraction patterns and intensity as that of fresh catalysts after 1200 h of operation at 350 °C, indicating catalysts were thermally stable. The results of the N₂-BET surface area measurements are summarized in Table 2 for fresh and KCl exposed catalysts. The surface area of the fresh VWT, Cu-HZSM5 and Cu-HMOR catalysts was found to be 64, 338 and 312 m²/g, respectively. Surface area of analogous KCl exposed catalysts was found to be 53, 274 and 260 m²/g. Such a decrease in surface area is due to specific interaction of potassium with the support as well as partial physical blocking of the support pores.

Fig. 4 shows NH₃-TPD profiles of fresh and potassium poisoned catalysts in the temperature range 100-600 °C. According to Topsøe et al. [22] chemisorption of NH₃ on the Brønsted acid V-OH site is important to activate the ammonia for the SCR reaction. It was also shown that the SCR activity and number of acidic sites are correlated for various catalysts [11, 12, 16]. The results of the NH₃-TPD measurements are summarized in Table 2. Fresh catalysts showed high intensity and broad NH₃-desorption patterns compared to the corresponding aerosol exposed catalysts. The total acidity of the fresh and poisoned catalysts were: Cu-HMOR > Cu-HZSM5 > VWT. Cu-HMOR and Cu-HZSM5 catalysts showed high initial acidity and even after KCl exposure the Cu-zeolite catalysts retained their acidity while the VWT catalyst showed

comparatively less initial acidity, and lost the majority of the acidic sites after KCl aerosol exposure.

The SCR activity of fresh and KCl aerosol exposed Cu-HMOR, Cu-HZSM5 and VWT plate type catalysts are shown in Fig. 5. Cu-HMOR, Cu-HZSM5 and VWT catalysts showed rate constant values at 350 °C of 94.3, 132.7 and 47.8 cm³/(g·s), respectively. The rate constants observed on these Cu-zeolites are 2-3 times higher than for commercial VWT catalyst. Probably due to the tuneable properties of the zeolite supports such as surface area and Si/Al ratio. The Cu-zeolite catalysts also showed enhanced activity compared to a commercial reference in the form of fractionized particles [11]. The observed superior activity of Cu-zeolites in both monolithic and powder forms might indicate that the coating procedure works very well.

Aerosol exposure measurements are more realistic and can give in depth knowledge about the deactivation phenomena. Aerosol exposed Cu-HMOR, Cu-HZSM5 and VWT catalysts showed rate constant values at 350 °C of 49.3, 56.0 and 2.3 cm³/(g·s), respectively. Hence, the commercial VWT catalyst showed little activity while the Cu-zeolites showed appreciable activity even after 1200 h of KCl aerosol exposure. Cu-HMOR and Cu-HZSM5 catalysts also showed high alkali resistivity in powder form after wet impregnation even at high K/Cu ratios of 0.80 and 0.64, respectively [11].

SEM-EDX analysis was used to investigate the surface structure and distribution of KCl on the surface and cross section of the plates in order to correlate the deactivation to the KCl concentration and depth of catalyst penetration. SEM surface images of the KCl exposed catalysts are shown in Fig. 6. The VWT and Cu-HMOR catalysts exhibited a homogeneous and smooth surface whereas the Cu-HZSM5 catalyst showed a more rough surface with fiber glass plate features. The SEM image of the catalysts at high magnification showed homogeneous distribution of KCl aerosol particles with an average size of around 0.4-0.7μm.

Table 3 shows the results obtained from elemental analysis performed on the catalysts by EDX with the active metal content (wt.%) and potassium/metal (mole/mole) ratio on the surface and along the wall thickness of the catalyst plate. The average metal content (Cu or V) is quite close to the theoretical value, as reported in Table 3. At the surface of the catalyst the potassium content was 3.5, 3.0 and 3.8 wt.% on Cu-HZSM5, Cu-HMOR and VWT catalysts, respectively. At a depth of 300 μm , the analogous potassium concentration was 0.33, 0.29 and 0.60 wt.%. These results indicate that almost similar concentration of potassium was present on the surface of the catalysts, and that the potassium diffusion rate across the catalyst walls was lower on Cu-HZSM5 and Cu-HMOR catalysts compared to the VWT catalyst.

At the surface of the catalyst the K/M ratio was 1.47, 1.25 and 3.14 on Cu-HZSM5, Cu-HMOR and VWT catalysts, respectively. There was a fast decrease in the potassium/metal ratio from the surface into the catalyst structure. Hence, at a depth of 700 μm an average potassium/metal ratio of about 0.14, 0.12 and 0.42 was found on Cu-HZSM5, Cu-HMOR and VWT catalysts, respectively. This confirms that the potassium is not only deactivating the surface of the catalyst, but also penetrates through the wall of the catalyst causing further deactivation. The penetration mechanism of potassium into the catalyst structure was explained by Zheng et al. [14] to be surface diffusion of the potassium deposited from the finest aerosol particles.

4. Conclusions

Deactivation of Cu-HMOR, Cu-HZSM5 and vanadium SCR catalysts by KCl aerosols has been investigated. Cu-HMOR and Cu-HZSM5 catalysts are highly active in SCR of NO with NH_3 and exhibited high resistance to potassium aerosols. SEM-EDX analysis revealed that potassium was present both on the surface and in the cross section of the catalyst wall. The K/M ratio across the wall of the catalysts was high on the vanadium catalyst (0.40-0.55) while the Cu-

zeolite catalysts had significant lower concentrations (0.20-0.14) in the wall. The results of the NH₃-TPD experiments showed that a small decrease in total acidity of the Cu-zeolites catalysts was obtained unlike the vanadium catalyst which exhibited a drastic decrease of the acidic sites. The high alkali deactivation resistance is attributed to the high surface area and acidity of the zeolite supports.

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List of tables

Table 1 Characterization of the support particles and coating stability.

Support	Si/Al	zeolite (wt%)	colloidal silica (wt%)	particle size (μm)			zeolite loss (wt.%)
				D _{0.1}	D _{0.5}	D _{0.9}	
HZSM5	15	20	5	1.5	3.6	8.0	48
HMOR	10	20	5	0.9	3.1	17.7	37

Table 2 Surface area and NH₃-TPD of catalysts.

Catalyst	BET Surface Area (m^2/g)		Acidity ($\mu\text{mol/g}$)	
	Fresh	KCl exposed	Fresh	KCl exposed
Cu-HZSM5	338	274	1349	1052
Cu-HMOR	312	260	1590	1399
VWT	64	53	364	160

Table 3 EDX analysis on the surface and cross section of the catalysts.

Catalyst	Metal	Potassium content (wt.%)			Potassium/Metal (mol/mol)		
		Content (wt.%)	Surface	300 μm	700 μm	Surface	300 μm
Cu-HZSM5	4 (3.9) ^a		3.5	0.33	0.25	1.47	0.24
Cu-HMOR	4 (3.8) ^a		3.0	0.29	0.21	1.25	0.21
VWT	1.7 (1.6) ^a		3.8	0.60	0.45	3.14	0.55

^a Metal content measured from EDX analysis on the surface of exposed catalysts.

Figure captions

Fig.1 Experimental setup of KCl aerosol exposure pilot plant.

Fig.2 Particle size distribution of HZSM5 (thick line) and HMOR (dotted line) used for coating suspensions.

Fig.3 XRPD patterns of fresh (thick line) and KCl aerosol exposed (dotted line) Cu-HMOR, Cu-HZSM5 and VWT catalysts.

Fig.4 NH₃-TPD profiles of fresh (thick line) and KCl aerosol exposed (dotted line) Cu-HMOR, Cu-HZSM5 and VWT catalysts.

Fig.5 SCR activity of fresh and KCl aerosol exposed Cu-HMOR, Cu-HZSM5 and VWT catalysts.

Fig.6 SEM surface images of KCl aerosol exposed Cu-HMOR, Cu-HZSM5 and VWT catalysts.

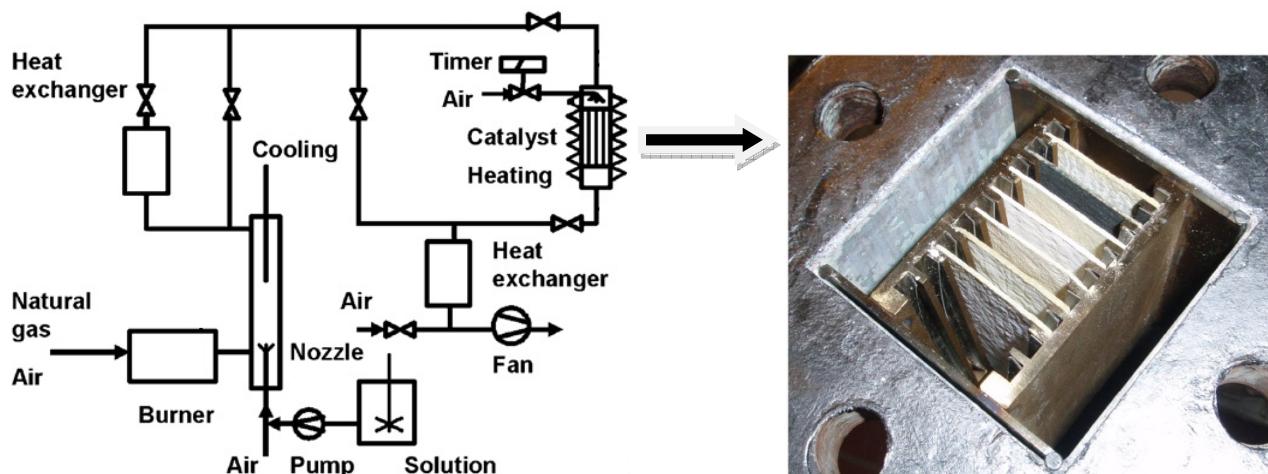


Fig. 1

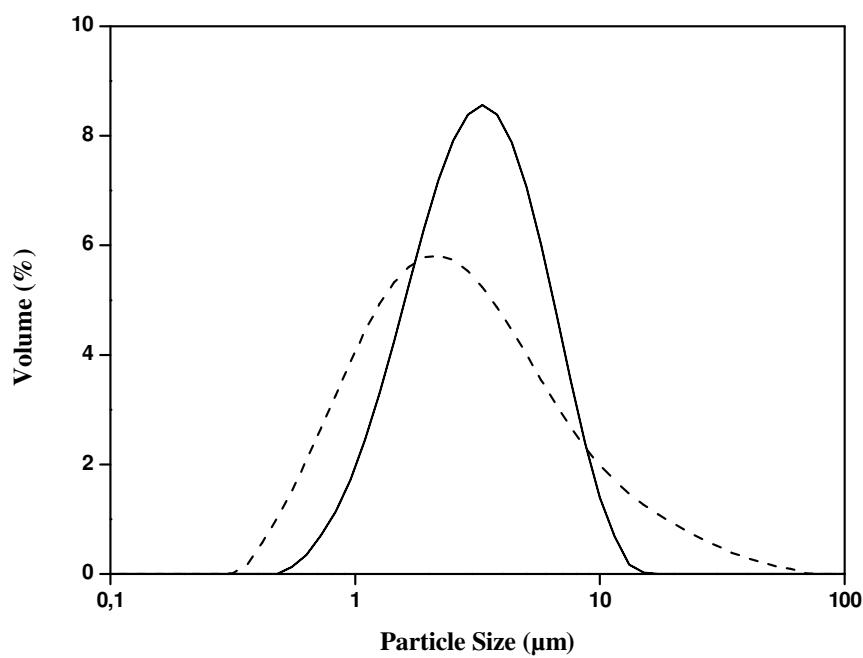


Fig. 2

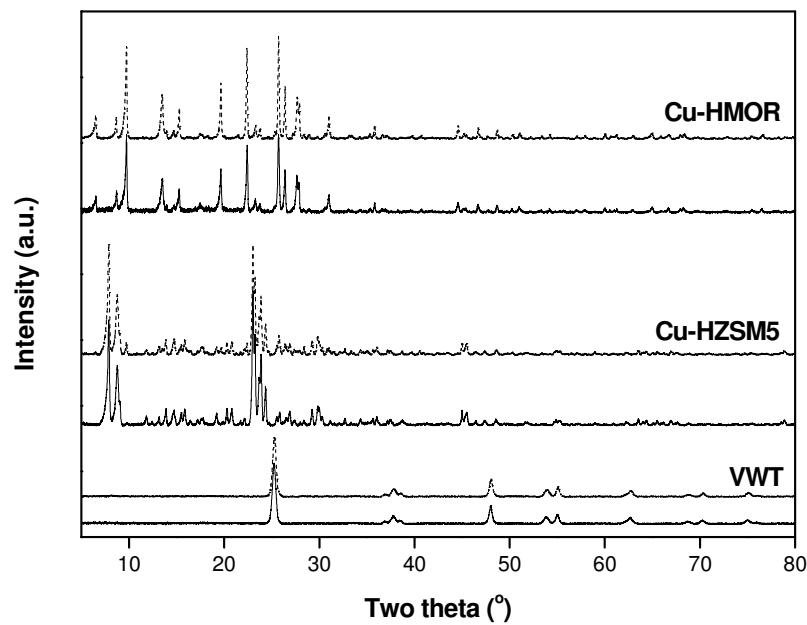


Fig. 3

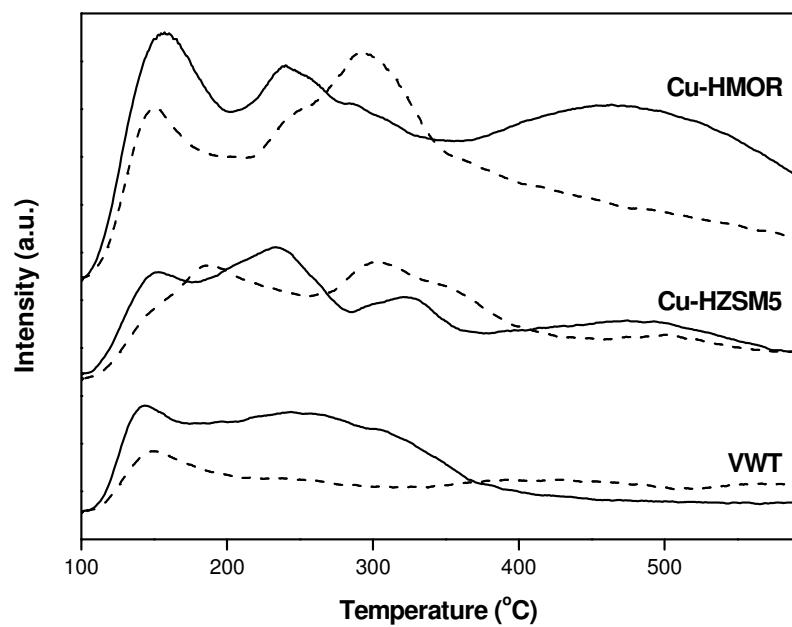


Fig. 4

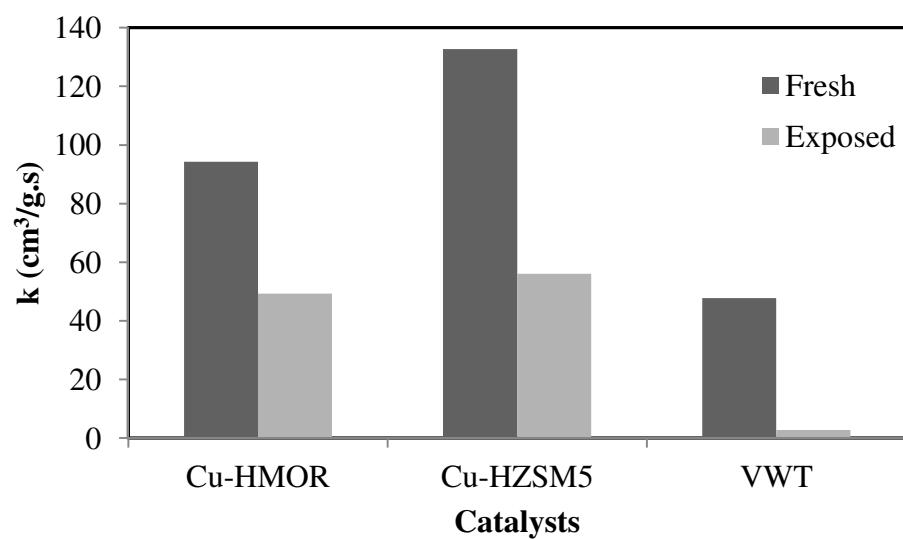
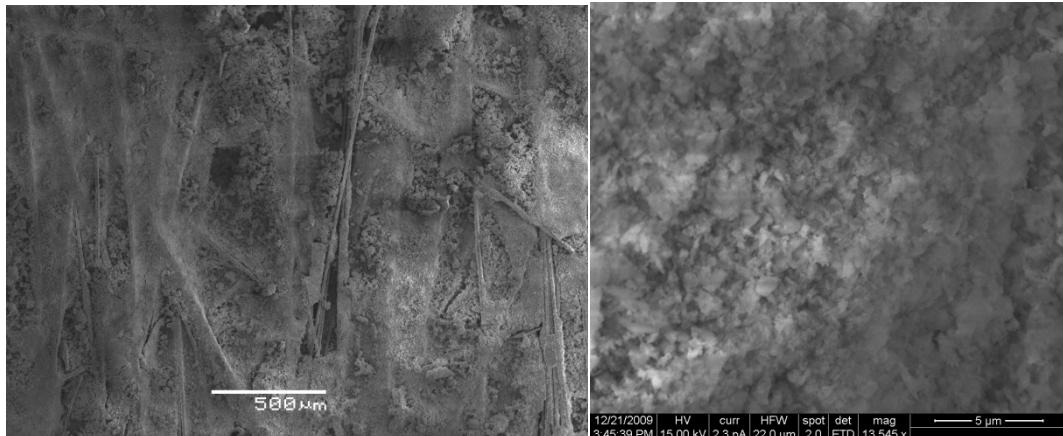
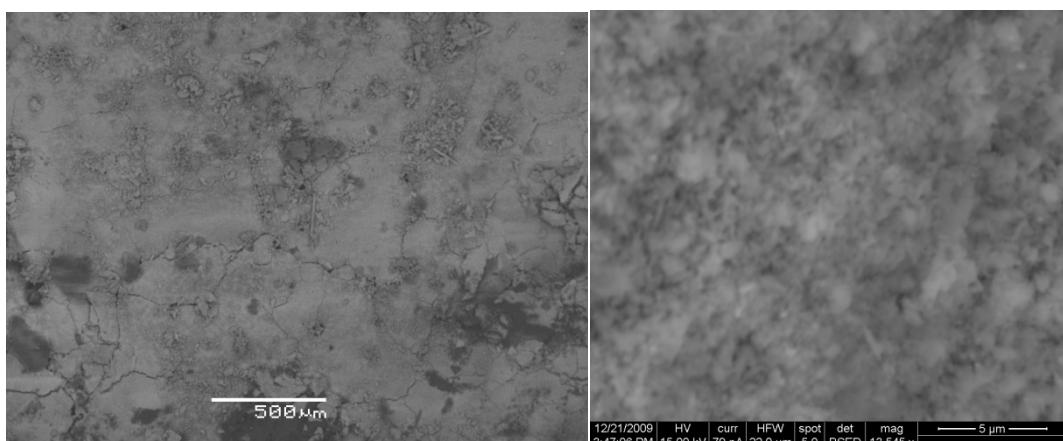


Fig. 5



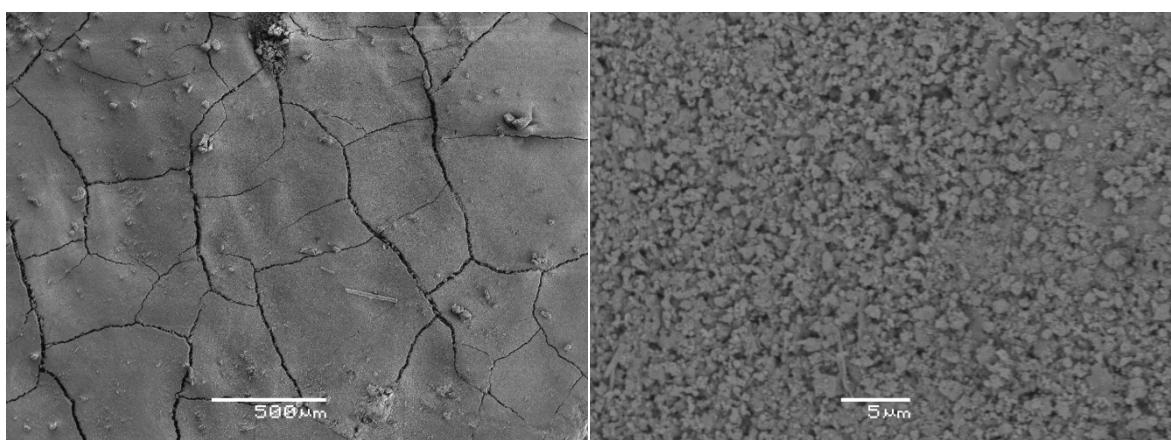
Cu-HZSM5

Cu-HZSM5



Cu-HMOR

Cu-HMOR



VWT

VWT

Fig. 6