

## Generation and reactivity of NiCr clusters

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### Introduction

Bimetallic alloy clusters of ubiquitous metals represent one of the most promising way towards new catalytic systems. Metal mixing (alloying) can significantly modify the catalytic activity and selectivity. However, how alloying modifies reactivity behavior is still an open question. Does it just change the cluster distribution of a given metal which otherwise retains its reactivity, or does it change the local bonding geometry (structure effect), or modify the reactivity of the metal atoms? This work is our first step toward the study of cationic NiCr bimetallic clusters which contains 70 wt% of Ni and 30 wt% of Cr. Since Kaldor and co-workers [1] published experimental data on generation of neutral NiCr alloy clusters in gas phase no experimental data are available according to our best knowledge. Moreover, in contrast to several theoretical published works, no data on NiCr oxide clusters in gas phase were published either.

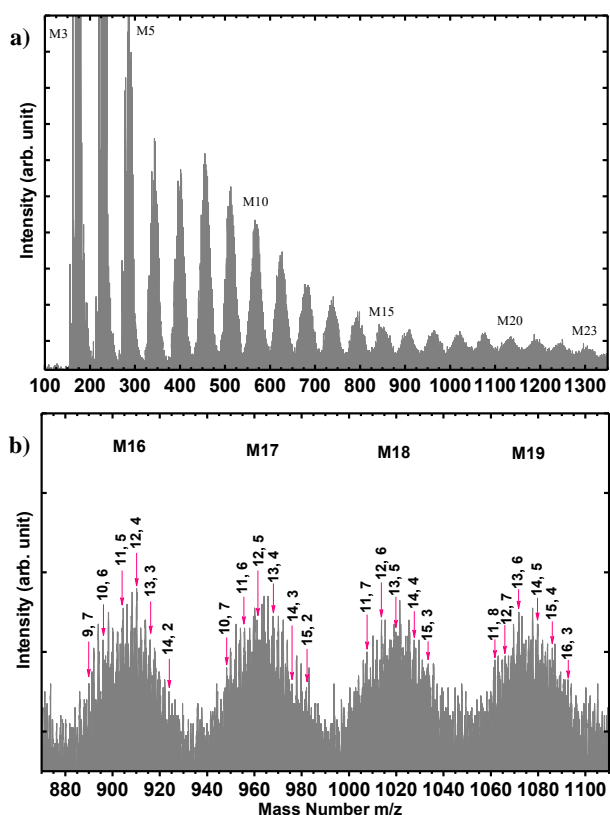
### Experimental

Experimental apparatus and measurement techniques have been described in details in previous work on nickel oxide clusters [2]. Briefly, NiCr alloy clusters were generated by laser vaporization of Ni<sub>0.7</sub>Cr<sub>0.3</sub> alloy rod within the supersonic beam from a solenoid pulsed valve and NiCr<sup>+</sup> cations were detected by using TOF-MS. Reaction with molecular oxygen and nitrous oxide were investigated, in order to reveal basic mechanism of reactivity of these bimetallic alloy cluster cations which can be a potential substitute to the widely used rare metal.

### Results and discussion

Figure 1 shows the experimentally observed cluster distribution of Ni<sub>x</sub>Cr<sub>y</sub><sup>+</sup> up to  $x + y = 23$  of total number of atoms in the clusters. Qualitative peak assignment of experimental data is well correlated with the alloy source component ratio (Ni<sub>0.7</sub>Cr<sub>0.3</sub>).

We examined the reactions of NiCr<sup>+</sup> cluster cations with molecular oxygen and nitrous oxide at minimum concentration where oxide products intensity is high enough to observe, and at high concentration where reactions are dominated by multi-collision with reactant gas.

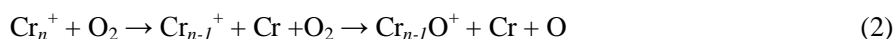


**Fig.1** Mass spectra of the Ni<sub>x</sub>Cr<sub>y</sub><sup>+</sup> alloy clusters: a) experimental spectrum with range M 3-23 of total number of cluster components, where  $M = x + y$ , b) spectrum with selected  $m/z$  range.

The initial stages of oxidation with 0.1 torr O<sub>2</sub> are favored formation of the cluster dioxides:

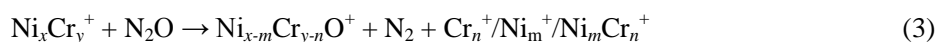


As the O<sub>2</sub> partial pressure of the reactant gas increase, the multioxides Ni<sub>x</sub>Cr<sub>y</sub>O<sub>z</sub> tend to be formed. It is well known in literature [3, 4] that the initial state of the oxidation of Cr<sub>n</sub><sup>+</sup> and Ni<sub>m</sub><sup>+</sup> clusters is the cluster dioxides formation, and with rising O<sub>2</sub> concentration the dominant products are switched to multioxides, which is similar to the NiCr case. However, the generation mechanism of Cr<sup>+</sup> and Ni<sup>+</sup> oxides is verified as the dissociative chemisorption mechanism, e.g.:



Comparing it with NiCr<sup>+</sup> oxidants formation, where even the same type of oxide products are formed in low and high oxygen concentration, no any evidence of dissociative chemisorption mechanism was observed in our experimental conditions. Moreover, as it is shown in reactivity map in Figure 2a for low O<sub>2</sub> concentration it seems to be a kind of “reactivity barrier” for the large clusters. Small Ni<sub>x</sub>Cr<sub>y</sub><sup>+</sup> clusters (x + y = 2-9) are much more reactive with molecular oxygen, which indicates the reactivity size dependence.

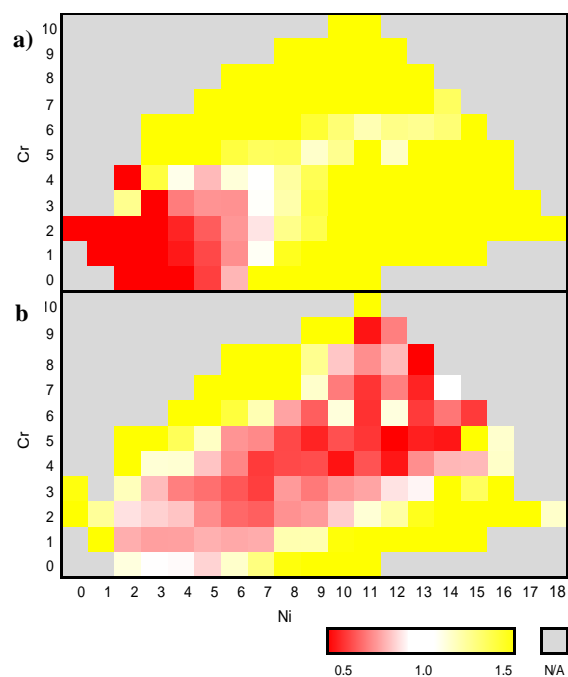
In the N<sub>2</sub>O case, oxygen transfer reaction was occurred:



It is clear that the clusters oxides formed even at minimum N<sub>2</sub>O concentration dissociate by sequential loss of chromium or nickel atoms or “cluster fragments”, Ni<sub>m</sub>Cr<sub>n</sub>, where n, m << x, y. Dissociative chemisorption of the atomic oxygen on the cluster surface heats the cluster strongly and dissociation ensues. Relatively high ratio of small Ni<sub>x</sub>Cr<sub>y</sub><sup>+</sup> clusters in Figure 2b is a result of rising number of “cluster fragments” by dissociative chemisorption in N<sub>2</sub>O reaction, while rich mono-oxides of these small NiCr<sup>+</sup> clusters was observed.

Moreover, by post heating experiment (experimental procedure was described in previous work as well [2]) were verified that oxygen are considered to bind strongly to NiCr<sup>+</sup>, which indicate that NiCr<sup>+</sup> oxides are stable structures even at high temperature conditions (up to ~500 °C).

NiCr cluster in gas phase have definitely different catalytical properties than their monocomponents Ni and Cr clusters, which make these bimetallic clusters developmental subject of future study.



**Fig.2** Color maps for the bare Ni<sub>x</sub>Cr<sub>y</sub><sup>+</sup> alloy clusters ratio of clusters integrated intensity: a) ratio with/without reaction with O<sub>2</sub>  $I_{\text{withO}_2}/I_{\text{withoutO}_2}$ , b) ratio with/without reaction with N<sub>2</sub>O =  $I_{\text{withN}_2\text{O}}/I_{\text{withoutN}_2\text{O}}$ . Partial pressure for O<sub>2</sub> and N<sub>2</sub>O was 0.1 and 1 torr, respectively.

1. E.A. Rohlffing, D.M. Cox, R. Petkovic-Luton, A. Kaldor, “Alloy cluster beams: nickel/chromium and nickel/aluminium”, J. Phys.Chem. 1984, 88(25), 6227-6231.
2. K. Sakuma, K. Miyajima, F. Mafuné, „Oxidation of CO by nickel oxide clusters revealed by post heating”, A, 2013, 117(16), 3260-3265.
3. J.B. Griffin, P.B. Armentrout, “Guided ion beam studies of the reactions of Cr<sub>n</sub><sup>+</sup> (n = 2-18) with O<sub>2</sub>: chromium cluster oxide and dioxide bond energies”, J. Phys. Chem., 1998, 108(19), 8062-8074.
4. D. Vardhan, R. Liyanage, P.B. Armentrout, “Guided ion beam studies of the reactions of Ni<sub>n</sub><sup>+</sup> (n = 2–18) with O<sub>2</sub>: Nickel cluster oxide and dioxide bond energies”, J. Chem. Phys. 2003, 119(8), 4166-4178