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Kinetic Analysis and Design of Catalytic Redox Cycles

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Highlights

- New approach of kinetic study of redox reaction by combined MS and in-situ UV-Vis-NIR spectroscopy
- New kinetic model for predicting both gas phase and catalyst composition evolution
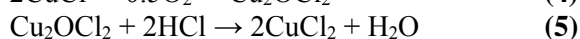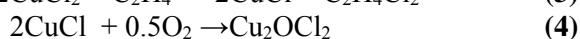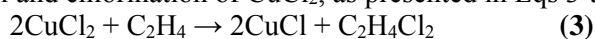- Rational design of catalysts guided by a rate diagram

1. Introduction

The oxidation reaction is one of the most important catalytic processes, playing an important role in numerous industrial, environmental and energy applications. All these reactions involve redox reactions where both reactants and catalysts undergo electron transfer reactions through reduction and oxidation. For a selective oxidation reaction, the main reaction mechanism is normally the Mars and van Krevelen mechanism, and the redox catalytic cycles can be simplified as:

$$[CatO] + R\text{-}C \rightarrow RC\text{-}O + [Cat] \quad \textbf{(1)}$$

$$[Cat] + 1/2\ O_2 \rightarrow RC\text{-}O \quad \textbf{(2)}$$
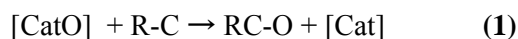
Where [CatO] represents the oxidized catalyst surface and [Cat] its reduced state. The active sites or oxidation state are entirely dynamic in nature and depend on the relative re-reduction and re-oxidation rates. The oxidation state of the catalysts and amount of lattice oxygen determine the activity, selectivity and stability. Many redox reactions involving C, Cl, N, and S follow similar simplified mechanism on metal carbide, chlorides, nitrides and sulfides. However, despite their great importance in industries, there are three main challenges hindering better understanding, prediction and control of these catalytic cycles, namely materials, active sites and kinetics challenges. The catalysts for redox reactions are typically multicomponent and/or multiphasic oxides, nitrides, or chlorides, in addition to existing of oxygen or other vacancy. The active site is fully dynamic, and the number and nature of active sites are not constant, depending on the reaction conditions and catalyst properties. The dynamic nature of the active sites have not been able to be taken into account in the typical kinetic models such as Langmuir-Hinswood model. Therefore, efficient methods and tools for diagnosing or monitoring, predicting and controlling the catalytic cycles are still missing. A tool for rational design and fine-tuning of the catalytic redox cycle is ugly desired to develop more active, selective and stable catalysts for redox reactions. Here we report a new approach for kinetic analysis and rational design of the redox reaction cycles as well as a new kinetic model for predicting evolution of catalyst and product composition at transient and steady-state reaction conditions. The application of the new approach in the two cases, namely ethylene oxychlorination on $CuCl_2$ and methane total oxidation on Ni-Co catalysts will be discussed.

1, 2 dichloroethane (EDC) is the intermediate for vinyl chloride monomer (VCM). Ethylene oxychlorination is the important industrial process to produce EDC. The ethylene oxychlorination reaction occurs in the catalytic cycle with three sequential reaction steps such as $CuCl_2$ reduction by ethylene to CuCl, CuCl oxidation to CuOCl and chlorination of $CuCl_2$, as presented in Eqs 3-5.

$$2CuCl_2 + C_2H_4 \rightarrow 2CuCl + C_2H_4Cl_2 \quad \textbf{(3)}$$

$$2CuCl + 0.5O_2 \rightarrow Cu_2OCl_2 \quad \textbf{(4)}$$

$$Cu_2OCl_2 + 2HCl \rightarrow 2CuCl_2 + H_2O \quad \textbf{(5)}$$

The activity and stability depend significantly on the ratio of Cu^{2+}/Cu^{+1}. Cu^{2+} is recognized as the active site and Cu^{1+} is not active but volatile. The kinetics of the redox catalytic cycle was developed by the transient

kinetic study of individual reduction and oxidation steps. The kinetics can predict not only the reactant conversion rates but also the evolution of catalyst oxidation state[1-3].

2. Methods

All $CuCl_2/\gamma$-Al_2O_3 catalysts were made according to the incipient wetness impregnation method from the chloride salts, containing 5wt% Cu and a promoter: Cu molar ration of 0.4. The catalyst physical properties was obtained with BET, catalyst characterization with *ex situ* XRD, XPS and Raman spectroscopy. The transient and steady-state kinetic studies were performed in a fixed bed reactor combining mass spectroscopy (MS), gas chromatograph (GC) and *in-situ* ultraviolet–visible-Near-infrared (UV-Vis-NIR) spectroscopy [1-2]. Reactants were fed at 230°C one by one in step transient experiments and effluent gasses monitored by an online MS and GC. The kinetics of reduction, oxidation and chlorination steps as well as steady-state ethylene oxychlorination were investigated separately.

3. Results and discussion

The reduction and oxidation steps in the redox cycle of ethylene oxychlorination on $CuCl_2/Al_2O_3$ were studied separately at different conditions, where the evolution of gas composition and Cu oxidation state with time on stream was measured by MS and UV-Vis-NIR, respectively. The calibrated UV-Vis-NIR spectroscopy allowed in-situ measurement of the Cu oxidation state at steady-state reaction conditions to take into account the dynamic changes in the number of active sites, which makes it possible to study the intrinsic site activity of catalysts. The spatial Cu oxidation state profiles were obtained by scanning the catalyst bed. Based on the developed methodology, spatial-time kinetic performance of the reaction steps in the catalytic cycle and promotor influence, i.e. Li, K, Na, Rb, Cs, Li Ce and K on the $CuCl_2/\gamma$-Al_2O_3 catalyst have been studied in terms of activity, selectivity and stability. The re-oxidation of Cu^+ by oxygen was found to be the limiting step leading to low Cu^{2+}/Cu^+ in the cycle on $CuCl_2/\gamma$-Al_2O_3. The kinetic model of the catalytic cycle was obtained by an integration of kinetics of reduction and oxidation steps by a steady-state assumption, and the model predicted well the evolution of gas phase and solid catalyst composition.

Moreover, a methodology for catalyst development when the catalyst partakes in redox reactions, is developed by using rate diagrams as a tool to taken into account of the microkinetics of the catalytic cycle at both transient and steady-state conditions. In a rate diagram, the reduction and oxidation rates are integrated together as a function of Cu^{2+} concentration, where the cross point reflects the steady-state reaction rate and Cu_{2+} concentration. With the guidelines of the catalyst design using the new rate diagram, mixed promoters has been identified, which not only increased the catalyst activity, but also remarkably improved the stability.

4. Conclusions

An approach combined transient and steady-state kinetic study with combined MS and UV-VIS.NIR spectroscopy is developed to study catalytic redox cycle to take into account the dynamic nature of the active sites. A new type of kinetic model has been suggested to adequately predict evolution of reactants and production as well as the oxidation state of the catalysts in catalytic cycle. In addition, the rate diagram is proposed to virtually illustrate the kinetic behaviors of the redox cycle, which is also applied as guidelines for rational catalyst design.

References

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Keywords
Redox catalysis, transient and steady-state kinetics, kinetic modeling, catalyst design