Oxygen transfer in mixed oxides in the case of CO oxidation over oxides containing Cu, Mo and V

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The combined measurement of reaction rate and oxygen activity in the catalyst by solid electrolyte potentiometry (SEP) can be used in principle to examine the concept of oxygen transfer in mixed oxides, often used to explain synergetic effects between different solid phases. This is shown in the case of copper molybdate and a Mo–V–O_x mixed oxide, using the oxidation of CO as a test reaction. Both the pure oxidic phases and a physical mixture are used in the study. The rate measurements show that the addition of Mo–V–O_x, inactive in CO oxidation, enhances the catalytic activity of $CuMoO_4$. On the other hand, SEP measurements indicate the existence of a gradient of oxygen activity between the two phases as the driving force of oxygen transfer from the Mo–V oxide to the copper molybdate.

Keywords: synergism, oxides, solid electrolyte potentiometry, *in situ*, oxygen transfer, oxygen acceptor (donor)

1. Introduction

Multicomponent oxidic catalysts are commonly used in the partial oxidation of hydrocarbons and other organic compounds [1]. The efficiency of such catalysts and the synergetic effects observed in the presence of a mixture of well defined oxides raise the question of their origin. Different explanations of these synergetic effects, which may result in the enhancement of both activity and selectivity, have been proposed [2–4]. Among these the remote control process [4], which is due to spill-over of oxygen from one oxide (donor phase) to another (acceptor phase), is widely used to explain such synergetic effects. From the results of kinetic measurements Delmon et al. suggested a ranking of several oxidic phases due to their potential of accepting or donating oxygen species [4].

The transfer of oxygen is a function of the phase composition of the catalyst, i.e., its oxidation state. Under operating conditions this oxidation state is not only determined by the oxygen partial pressure in the gas phase but results from the rates of oxygen transfer to and from the solid. Thus, there is a mutual interaction of the gas phase and the solid catalyzing the gas-phase reaction.

To characterize the oxidation state of a solid, Wagner [5] proposed the measurement of its oxygen activity by a potentiometric method, the solid electrolyte potentiometry (SEP). It is based on the use of an ion-conducting solid as electrolyte.

In the following, we present experimental results of the CO oxidation over oxidic catalysts mainly containing Mo, V and Cu. Oxidic phases of these elements are the main constituents of many catalysts used for the partial oxidation of hydrocarbons. Kinetic measurements over a fixed bed of the pure phases $CuMoO_4$ and Mo–V–O_x, on one hand, and a physical mixture of these two phases, on the other hand, should indicate whether synergetic effects occur in this system. Potentiometric measurements (SEP) under reaction conditions were carried out simultaneously with the aim of confirming the oxygen transfer inside such multicomponent oxidic catalyst as the reason for synergetic effects. The CO oxidation has been chosen as a model reaction due to its simple stoichiometry.

2. Experimental

The experimental set-up (figure 1) can be divided into two parts, the fixed-bed reactor for kinetic measurements and a second device for the SEP.

The pure-oxidic phases $CuMoO_4$ and Mo–V–O_x used throughout the study have been described in detail elsewhere [6,7]. The physical mixture was obtained by mixing the powder of the pure phases for 1 h in a ball mill at a mass ratio $m_{CuMoO_4}/m_{Mo–V–O_x}$ of $1/8$.

The feed was composed of O_2, CO and N_2. The molar ratio of either CO or O_2 at reactor outlet was kept constant at 2% while the molar ratio of the other compound was stepwise increased from 1 to 5%. The composition of the feed could be analysed by bypassing the fixed-bed reactor. The concentrations of CO_2 and CO were determined by using infrared photometers (Rosemount, Binos 1), the O_2 concentration was measured by a magnetomechanic device (Hartmann and Braun, Magnos 3).

The kinetic experiments were carried out in a tubular reactor (210 mm length, 12 mm i.d.) at a pressure of 1.2 bar and a temperature of 300 °C. The first part of the reactor

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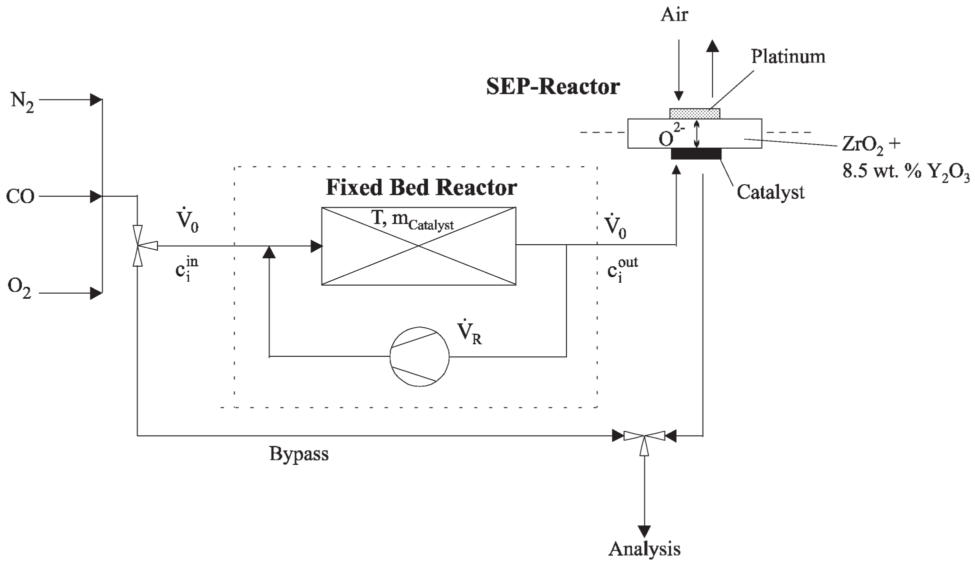

Figure 1. Schematic diagram of the used set-up.

consisted of a bed of glass spheres (100 mm length, 2 mm particle diameter) for heating the reactants to reaction temperature. A bed of catalyst (50–80 mm length) consisting of 5–8 g of a sieve fraction (0.63–0.9 mm) was employed.

The fixed-bed reactor is part of a gradientless recirculation system. The system is open to atmosphere, its recirculation ratio $\dot V_R/\dot V_0$ has a value of 48 at a volume flow rate of $\dot V_0 = 90$ ml/min NTP. Thus the concentrations in the reactor and at the outlet of the system are identical. The dotted lines in figure 1 show the boundaries of the control volume. The mass specific reaction rate r_m is obtained via the mass balance of the open system in stationary state:

$$r_m = \frac{1}{m_{catalyst}} \dot V_0 c_{CO_2,out}. \quad (1)$$

The principles of the SEP measurements have been described in detail elsewhere [8]. The unerlying assumptions for its use in the case of oxidic catalysts have equally been discussed [9]. The galvanic cell consisted of a solid electrolyte disk (thickness 2 mm) made of zirconia stabilized with yttria (8.5 wt%), which was coated with the oxidic catalyst on the measuring side, and with a porous platinum electrode on the reference side. The two porous electrodes of the galvanic cell are separated gas-tight by the solid electrolyte. The measuring electrode in the SEP cell consisted of the same catalyst powder which was used to prepare the sieve fraction for kinetic measurements. It was mixed with an organic binder [10] giving a viscous paste. The solid electrolyte was coated with this paste up to a film thickness of 300 μm and sintered for 1 h at 320 °C, leading to a sufficient adherence of the porous electrode on the electrolyte. The reference electrode was prepared by coating the electrolyte with a thin layer (80 μm) of a commercial platin paste (Demetron GmbH, M8014) and sintering the film for 2 h at a temperature of 800 °C.

The reactant mixture which had passed the fixed-bed reactor was contacted with the catalyst electrode of the SEP cell in order to characterize the oxidation state of the catalyst. CO conversion in the cell was always below 5% due to the minimized mass of the catalyst electrode. Thus, the composition of the gas phase in the catalyst bed and at the catalyst electrode was approximately equal and the measured potential difference between the electrodes was characteristic for the state of the catalyst in the fixed-bed reactor. Temperature and pressure in the cell were the same as in the fixed-bed reactor. The reference electrode was flushed with air. Both electrodes were connected with a high ohmic voltmeter. The measurement of the potential difference between these two electrodes leads to the value of the oxygen activity in the catalyst which is operationally defined by this method.

If the gas phase over measuring and reference electrode is only composed of oxygen and inert gases the cell will reach equilibrium after a certain time. In this case the correlation between the measured potential difference ΔE^* and the oxygen partial pressures at reference $p^{Ref}_{O_2}$ and measuring side $p^{Meas}_{O_2}$ is expressed by the Nernst equation:

$$\Delta E^* = -\frac{RT}{4F} \ln \frac{p^{Meas}_{O_2}}{p^{Ref}_{O_2}}, \quad (2)$$

where F is the Faraday constant ($F = 96486\ \mathrm{C\,mol^{-1}}$). The relation is based on the potential determining reaction:

$$O_{2,g} + 4e^-_{(Electrode)} \rightleftharpoons 2O^{2-}_{(Electrolyte)}$$

Under equilibrium conditions the oxygen activity in the solid is equal to the oxygen partial pressure at the measuring side:

$$a^2_O \equiv p^{Meas}_{O_2}. \quad (3)$$

Under reaction conditions, the oxygen activity a^2_O in the catalyst is operationally defined by the potentiometric measurement. Its value is related to the experimentally determined potential difference ΔE via the modified Nernst equation:

$$\Delta E = -\frac{RT}{4F}\ln\frac{a_O^2}{p_{O_2}^{\mathrm{Ref}}}. \tag{4}$$

3. Results and discussion

3.1. Equilibrium conditions

Measurements under equilibrium conditions were performed by initially contacting reference and measuring electrode with synthetic air and stepwise increasing the cell temperature until a stationary potential difference of 0 ± 5 mV was attained within minutes. The as-determined temperature T_l represents the lower temperature limit for equilibrium measurements as polarization effects inhibit the formation of a stable potential at lower values. In the case of copper molybdate T_l was found to be equal to 763 K, the respective value for the Mo–V–O_x electrode was 683 K. At these temperatures the oxygen partial pressure at the measuring side was then stepwise decreased in the following. Figure 2 shows the measured (symbols) and calculated potential differences (line), the latter being obtained by use of the Nernst equation (2). The good agreement between measured and computed values is a hint to the proper arrangement of the SEP cell.

Under reaction conditions the temperature limit of SEP measurements is different and may lay well below the equilibrium values. An operational definition has been proposed recently by Lintz et al. [11]. In the present case, under reaction conditions SEP can be safely applied at 573 K.

3.2. Copper molybdate under reaction conditions

Typical results of the combined kinetic and potentiometric measurements over the copper molybdate are shown in figure 3. The experimentally determined values of the reaction rate (left diagram) and the oxygen activity (right diagram) are plotted versus the concentration of CO (triangles) and O_2 (squares), while the respective molar fraction of the other component was kept constant at 2%, that is, 0.5 mol/m^3.

The reaction rate increases with rising concentration of CO and O_2 indicating a reaction order higher than zero with respect to either of these components. The reaction order with respect to CO is higher than that with respect to O_2, as can be seen from the slope of the reaction rate curve. For high oxygen concentrations the reaction rate tends to a constant value which seems to indicate that the interaction of CO with the surface becomes the rate determining step.

The oxygen activity (or oxygen content) increases with rising oxygen concentration due to the higher amount of oxygen adsorption. The decrease of the oxygen content with rising CO concentration is caused by the increasing rate of oxygen removal from the catalyst due to oxidation of CO to CO_2.

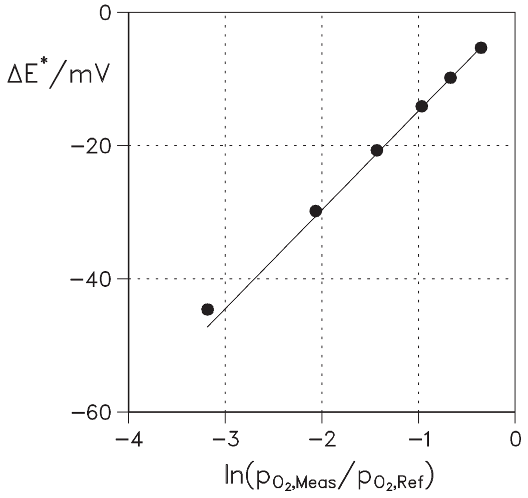

Figure 2. Measured (symbols) and calculated (line) potential differences under equilibrium conditions as a function of $\ln(p_{O_2,\mathrm{Meas}}/p_{O_2,\mathrm{Ref}})$; catalyst Mo–V–$O_x$; $T = 688$ K; $p_{O_2,\mathrm{Ref}} = 0.205$ bar.

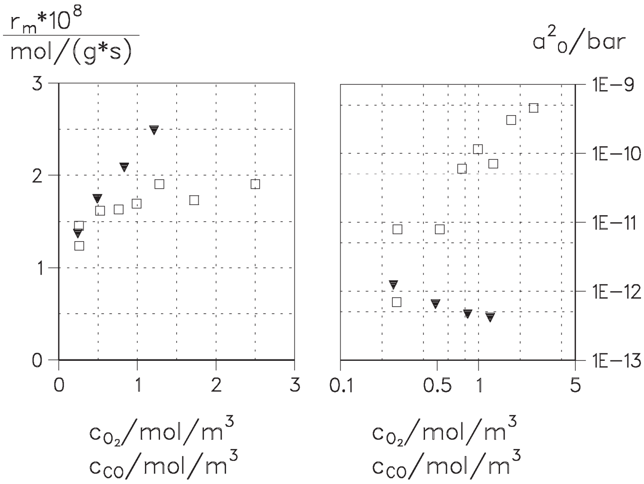

Figure 3. Reaction rate (left diagram) and oxygen activity (right diagram) as a function of the oxygen or CO concentration; catalyst $CuMoO_4$; $T_R = 573$ K; (□) $x_{CO} = 2\%$, (▼) $x_{O_2} = 2\%$.

The values of the oxygen activity are about eight orders of magnitudes lower than the partial pressure of the oxygen in contact with the catalyst, clearly indicating that oxygen in the gas phase and oxygen in $CuMoO_4$ are not in equilibrium. Quasi-equilibrium of chemisorption, that is the oxygen activity at the solid is equal to the partial pressure of oxygen, is only attainable if the virtual maximum rate of chemisorption is much larger than that of consumption by the oxidation. Therefore, we may call this case "slow reaction", but it is not realized at $CuMoO_4$.

3.3. Mo–V–O_x under reaction conditions

Under the applied reaction conditions the oxide showed no catalytic activity. Thus the limit case of an extremely "slow reaction" is obtained and we expect equilibrium between gas phase and chemisorbed oxygen. However, at 573 K we are well below the limit temperature T_l and SEP measurements under equilibrium conditions should be impossible. In fact, no stable values of the potential difference could be obtained in the galvanic cell thus confirming our expectations. If the temperature limit T_l of Mo–V–O$_x$ were below 573 K we would expect the value of the potential difference ΔE predicted by the Nernst equation (2) even under reaction conditions.

3.4. The physical mixture Mo–V–O$_x$/CuMoO$_4$ under reaction conditions

The results of the simultaneous kinetic and potentiometric measurements for the physical mixture Mo–V–O$_x$/CuMoO$_4$ are similar to those obtained for the pure CuMoO$_4$.

The oxygen activity of the mixture rises with increasing oxygen and decreasing CO concentration, the values being higher for the mixture than for the pure copper molybdate. The values of the reaction rate, reported in figure 4, are related to the total mass of the catalyst mixture which contains merely 11% of the active compound CuMoO$_4$ and 89% of the catalytically inert material Mo–V–O$_x$. The latter should act as a simple diluting material if it remained inert in the mixture. Therefore, it is adequate to compare rate values related to the mass of CuMoO$_4$, both in case of pure molybdate and in the mixture of both oxides. This is shown in figure 5 and it is evident that the addition of Mo–V–O$_x$ to CuMoO$_4$ increases the reaction rate by a factor of 3, indicating a strong synergism between both phases.

The observed synergism can easily be explained by oxygen transfer as, e.g., proposed in the model by Delmon et al. [4]. In the present system CuMoO$_4$ represents the oxygen acceptor phase with active sites for CO oxidation which becomes reduced when a mixture containing CO is applied. Mo–V–O$_x$, when contacted with copper molybdate, can act as a donor phase which is able to transfer oxygen species to CuMoO$_4$, thus reoxidizing the reduced active sites on the acceptor phase CuMoO$_4$. The donor phase Mo–V–O$_x$ itself may be partially reduced during this process and becomes reoxidized by gas-phase oxygen.

The results of the potentiometric measurements confirm the proposed model if we suppose that pure Mo–V–O$_x$ is in quasi-equilibrium with the gas-phase oxygen even under reaction conditions. Therefore, the oxygen activity in Mo–V–O$_x$ is higher than in pure CuMoO$_4$ (oxygen sink), thus providing a gradient in the oxygen activity when a mixture of both phases is subjected to reaction. Along this gradient oxygen can be transferred from the Mo–V oxide to the copper molybdate, as shown in figure 6, resulting in an oxygen activity for the mixture that must lie between those at the single phases.

The right diagram in figure 5 confirms this hypothesis. The oxygen activity measured in the mixture is indeed always one order of magnitude higher than in the pure copper molybdate, but several orders of magnitude lower than in the pure Mo–V oxide (equilibrium value) strongly pointing to an oxygen transfer process between both oxides in the physical mixture. This process may also be regarded as the reason for the observed synergetic effect.

SEP measurement does not allow to distinguish between oxygen spill-over on the catalyst surface or oxygen transfer from one solid oxide to the other (cf. figure 6).

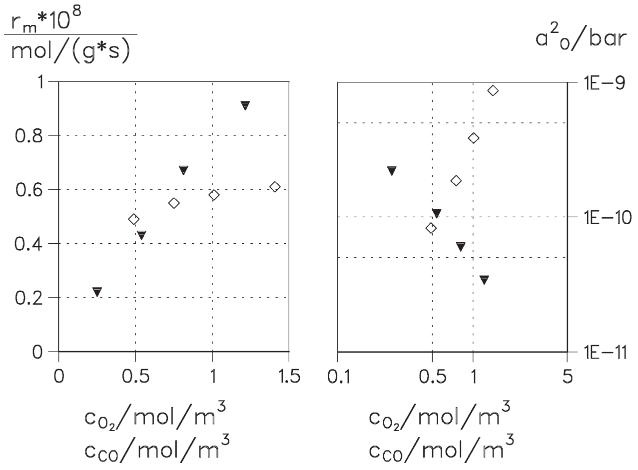

Figure 4. Reaction rate (left diagram) and oxygen activity (right diagram) as a function of the oxygen or CO concentration; catalyst CuMoO$_4$/Mo–V–O$_x$; T_R = 573 K; (◇) x_{CO} = 2%, (▼) x_{O_2} = 2%.

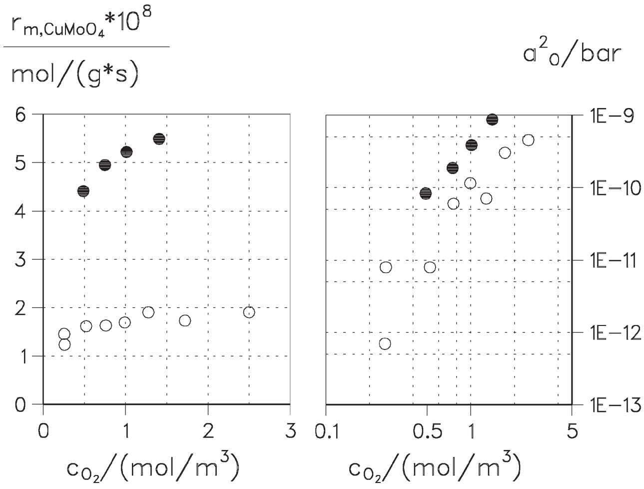

Figure 5. Reaction rate related to the mass of CuMoO$_4$ (left diagram) and oxygen activity (right diagram) as a function of the oxygen concentration; pure CuMoO$_4$ (○), CuMoO$_4$/Mo–V–O$_x$ (●); x_{CO} = 2%; T_R = 573 K.

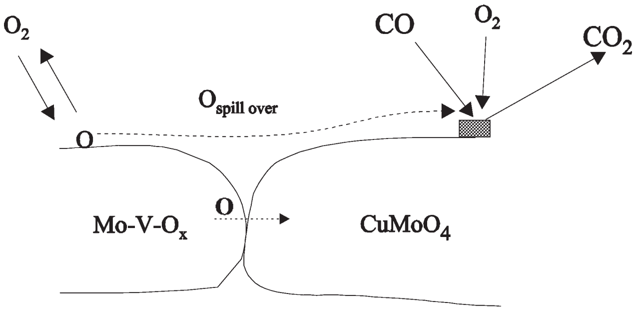

Figure 6. Oxygen transfer in mixed oxides.

Furthermore, SEP provides a possibility of confirming the ranking of oxygen acceptors and donors suggested by Delmon [4]. Following the above-mentioned concept, strong oxygen acceptors should correspond to low values of oxygen activity, strong oxygen donors to high values when exposed to the same reactant mixture.

Other explanations for the synergetic effect, as, for example, spreading of $CuMoO_4$ over the surface of Mo–V–O_x, cannot be excluded by the SEP measurements. The phenomenon of spreading is well known in the case of MoO_3 on the surface of alumina or V_2O_5 on titania [12]. Following this concept, $CuMoO_4$ might spread over the surface of the inert compound Mo–V–O_x leading to an increase of $CuMoO_4$ dispersion and thus to a higher surface of $CuMoO_4$, which could also explain the observed increase of the reaction rate. The Tammann temperature for copper molybdate $CuMoO_4$,

$$T_{\text{Tam}} \approx 0.5 T_{\text{melt,bulk}}, \tag{5}$$

which is considered to be sufficient to make atoms or ions of the bulk of a solid sufficiently mobile for bulk-to-surface migrations is equal to 561 K. So, spreading of $CuMoO_4$ might occur under the applied temperature of 573 K.

However, the mere increase of the $CuMoO_4$ surface by spreading should not enhance the oxygen activity in the catalyst, as observed experimentally. Therefore, even if we cannot totally exclude spreading, the SEP measurements show that oxygen transfer between both solids really takes place.

References

[1] J. Haber, Stud. Surf. Sci. Catal. 72 (1992) 279.
[2] J.M.M. Millet, H. Ponceblanc, G. Goudurier, J.M. Herrmann and J.C. Vedrine, J. Catal. 142 (1993) 381.
[3] O. Legendre, Ph. Jäger and J.P. Brunelle, Stud. Surf. Sci. Catal. 72 (1992) 387.
[4] B. Delmon and L.T. Weng, Appl. Catal. A 81 (1992) 141.
[5] C. Wagner, Adv. Catal. 21 (1970) 323.
[6] H. Werner, O. Timpe, D. Herein, Y. Uchida, N. Pfänder, U. Wild and R. Schlögl, Catal. Lett. 44 (1997) 153.
[7] M. Wiesmann, H. Ehrenberg, G. Miehe, T. Penn, H. Weitzel and H. Fuess, J. Solid State Chem. 132 (1997) 88.
[8] H.-G. Lintz and C. Vayenas, Angew. Chem. Int. Ed. Engl. 28 (1989) 708.
[9] H.-H. Hildenbrand and H.-G. Lintz, Ber. Bunsenges. Phys. Chem. 95 (1991) 1191.
[10] J. Brück, Dissertation, Karlsruhe (1995).
[11] J. Brück, H.-G. Lintz and G. Valentin, Solid State Ionics 112 (1998) 10.
[12] H. Knözinger and E. Taglauer, Specialist Periodical Report 10 (1993) 1.