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On the activation energies of the forward and reverse water–gas shift reaction

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Published experimental results demonstrate that the reverse water–gas shift reaction is surprisingly fast over several varied catalysts (metallic and oxidic). The observed values of activation energy of the reaction are shown here to be inconsistent with values calculated from the standard enthalpy change and the activation energies of the forward reaction. Possible explanations of this paradox are discussed in terms of the limits to the application of the "principle of microscopic reversibility" to catalytic systems.

Keywords: water–gas shift reaction; microscopic reversibility; activation energy; metal catalysts; oxide catalysts

1. Introduction

Although the forward water–gas shift reaction,

$$CO + H_2O \rightleftharpoons CO_2 + H_2 , \tag{1}$$

has been studied [1] for many years over both metal and oxide catalysts, the reverse reaction has attracted little attention. This was due partly to the formation of alcohol or hydrocarbon by-products over many catalysts, and partly to low equilibrium conversions under experimentally convenient conditions. Recently, the reverse reaction has been examined by several groups, using a variety of different catalysts, so some comparison of the forward and reverse reactions over several catalysts is now possible. In this paper we show that a striking feature of this comparison is the unexpectedly low activation energies (often coupled with high reaction rates) of the reverse reaction. Apparent discrepancies in the application of the "principle of microscopic reversibility" are examined, as are implications for the mechanism of the water–gas shift reaction.

2. Kinetics of the reverse water–gas shift reaction

Some kinetic parameters of the reverse water–gas shift reaction over various catalysts are given in table 1. In some cases other products were formed concurrently

Table 1
Kinetic parameters for the reverse water–gas shift reaction

Catalyst	Temperature range (K)	Activation energy ($kJ\,mol^{-1}$)	Comments	Ref.
$Cu/ZnO/Al_2O_3$	443–533	110		[2]
Cu/Al_2O_3	–	110	from temperature-programmed reaction spectroscopy	[3]
Cu/ZnO	495–560	80–90	low surface area catalysts	[4]
Cu/ZrO_2	473–533	93.2 ± 2.9		[5]
Pd/Al_2O_3	513–548	73		[6]
$Pd/CeO_2/Al_2O_3$	513–548	74		[6]
Pt/carbon	573–673	55–60		[7]
Pt–Ca/carbon	573–673	50		[7]
Pt–Mg/carbon	573–673	75		[7]
FeSi	523–673	67,72	iron silicates, calcined	[8]
FeSi-H	523–673	81,87	H^+ forms of FeSi	[8]
FeSi-K	523–673	68,98	K^+ forms of FeSi	[8]
ZnO	495–560	75–80	low surface area catalysts	[4]
Fe_3O_4/Cr_2O_3	600–700	~ 80	commercial catalyst	[9]
Fe_3O_4	600–700	~ 80		[9]

but the data refer only to the reverse water–gas shift reaction. A notable feature of the results is the comparatively narrow range of values of activation energy over both metal and oxide catalysts. Further, these values are low compared with the experimental activation energies of the forward reaction. In some cases at least the rates of reaction were unexpectedly fast, showing that some form of compensation effect does not seem to operate here.

The activation energy of the reverse water–gas shift reaction can be calculated by use of the ample experimental data for the forward reaction together with values of the standard enthalpy change for the reaction. Some calculated values are given in table 2. The values of ΔH° used were calculated for the temperature at the middle of the experimental temperature range. In only one case, the results for Cu/Al_2O_3 catalysts, are the experimental and calculated values of the activation energy in agreement. In all other cases the calculated values are much higher than the experimental values, with, for Fe_3O_4-containing catalysts, calculated values higher by a factor of about 2. Clearly these differences are beyond experimental error and consistent for several metal catalysts and oxide catalysts.

3. Principle of microscopic reversibility

The calculations in section 2 of the activation energies of the reverse water–gas shift reaction depend implicitly on the principle of microscopic reversibility (PMR). This can be expressed as: "... under equilibrium conditions, any molecular

Table 2
Kinetic parameters for the forward water–gas shift reaction and calculated activation energies for the reverse water–gas shift reaction

Catalyst	Mean temperature (K)	Activation energy (kJ mol^{-1})	Calculated activation energy for reverse reaction (kJ mol^{-1})	Ref.
Cu/Al_2O_3	653	55.6 ± 3.3	96	[10]
$Cu/ZnO/Cr_2O_3$	573	112	151	[11]
Pd/Al_2O_3	653	79.8 ± 2.9	118	[10]
Fe_3O_4/Cr_2O_3	598	129.4 ± 2.1 [a]	168	[12]
Fe_3O_4/Cr_2O_3	638	121.8 [b]	160	[12]
Fe_3O_4/Cr_2O_3	600	122	161	[13]
Fe_3O_4	642	106	144	[14]
ZnO	688	118	156	[14]
ZnO/Cr_2O_3	–	81.2	120	[15]
ZnO/Al_2O_3	658	67	105	[16]
ZnO/SiO_2	688	70	108	[16]
$ZnFe_2O_4$	692	103	141	[14]
MgO	688	116	154	[14]

[a] Crushed catalyst.
[b] Catalyst pellets; calculated with allowance for mass transfer.

process and the reverse of that process will be taking place on the average at the same rate..." [17]. There are limits to its application in catalytic reactions [18,19]. Strictly, PMR is valid only for molecular species at equilibrium [17]. Most, if not all, of the experimental values in tables 1 and 2 were obtained at low conversions, far from equilibrium, so the calculation and comparison of values of activation energies is not necessarily valid. Problems from the use of PMR in catalytic systems can, in practical terms, arise in at least two ways. First, in reaction mixtures of different compositions the reaction mechanisms of forward and reverse reactions may be different as will then be the appropriate kinetics. Thus measured activation energies may correspond to different reaction steps. Second, and perhaps of more general importance in catalysis, the nature of a heterogeneous catalyst (from bulk composition to surface structure) can be determined by the composition, etc. of the reacting mixture. Thus measurements of rates of forward and reverse reactions far from equilibrium over nominally the same catalyst are often in practice over different catalysts, so invalidating the use of PMR.

Clearly the water–gas shift reaction, over all the catalysts tested in table 1 (with the possible exception of copper catalysts), provides examples of this failure. The mechanistic implications are considered below. However, this type of discrepancy would not hold for any rate measurements on the water–gas shift reaction made at equilibrium. PMR would then be expected to be applicable, with forward and reverse activation energies related by the standard enthalpy change for the reaction.

4. Mechanism of the water–gas shift reaction

Two types of mechanisms have been proposed for the water–gas shift reaction over various catalysts, the associative and the regenerative [20]. In the associative mechanism a surface complex, usually identified as formate, is the reaction intermediate, e.g.,

$$CO + H_2O \rightleftharpoons \text{(intermediate)} \tag{1}$$

$$\text{(intermediate)} \rightleftharpoons CO_2 + H_2 \tag{2}$$

In the regenerative or redox mechanism the reactants separately oxidise or reduce the catalyst surface:

$$H_2O + * \rightleftharpoons H_2 + O(a) \tag{3}$$

$$O(a) + CO \rightleftharpoons H_2O + * \tag{4}$$

The oxygen species O(a) in reactions (3) and (4) may be either lattice oxygen, as in Fe_3O_4 catalysts, or adsorbed oxygen, as on Cu metal catalysts. There is much experimental evidence that the forward and reverse reactions may proceed by either mechanism, dependent on catalyst and reaction conditions [20]. Chinchen and Spencer [21] have suggested that, for catalysts and conditions where the energetics allow the regenerative mechanism to operate, this mechanism is faster than any associative mechanism.

Thus we can suggest three possible causes for the apparent failure of the principle of microscopic reversibility:

(a) There is a different mechanism for the reaction under forward and reverse conditions away from equilibrium. In view of the fast rates of the reverse reaction, a possibility is that in some cases the forward reaction proceeds via an associative mechanism and the reverse reaction by a redox mechanism. This would fit observations with ZnO catalysts. However, this cannot be the case with magnetite catalysts, where a redox mechanism is well established for the forward reaction [20].

(b) There is a change in the rate-determining step for the reaction under forward and reverse conditions away from equilibrium. The two observed activation energies then no longer apply to the same reaction step.

(c) The steady states of the catalyst are different under forward and reverse conditions, i.e. the reaction is not occurring on a common catalyst and so no simple relation between activation energies can be expected. One possible cause could be the very different partial pressures of water for small conversions. Depending on total pressure, typically $p_{H_2O} \geqslant 0.5$ bar for the data for the forward reaction, whereas conditions remain essentially dry for the reverse reaction. Thus very different extents of surface hydration can be expected under forward and reverse conditions.

The changes in surface hydration may also provide an explanation of the unexpectedly high rates of the reverse reaction. The lower surface coordination to be expected on oxide surfaces under dry conditions could well provide sites of higher activity either for CO_2 dissociation or for the production of surface formate.

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