Catalysis Letters Vol. 95, Nos. 3–4, June 2004 (© 2004)

Effect of residual chlorine on Ir-catalyzed reaction of solid CaO with gas mixtures of methane and water vapor

Masanori Suehiro*, Emi Ueda, Suzu Maguchi, Takafumi Konishi, and Noritetsu Yoshida

Department of Chemistry, Faculty of Science, Kobe University Rokkodai, Nada-ku, Kobe 657-8501, Japan

Received 6 November 2003; accepted 24 March 2004

The effect of residual chlorine on the metal-catalyzed reaction of solid calcium oxide with a gas mixture of methane and water vapor ($CaO + CH_4 + 2H_2O \rightarrow CaCO_3 + 4H_2$) is investigated at temperatures in the range 613–713 K, using solid samples of Ir/CaO prepared by TPR of $Ir/CaCO_3$ with different chlorine contents below 1.1%. Chlorine-containing samples exhibit anomalous reaction curves characterized by the initial slow and linear progress followed by abrupt acceleration, while chlorine-free samples react more rapidly from the beginning to give simple curves without any acceleration. In both cases, apparent activation energy of 170–190 kJ/mol and reaction order of 0.8–1.0 with respect to methane pressure are determined, demonstrating that the presence of chlorine does not affect the kinetics of the reaction. Thus, the large difference in initial rate is considered to reflect the inhibiting role of residual chlorine. Based on these findings together with the data on surface properties of Ir/CaO, a model is proposed to explain the accelerative progress observed when residual chlorine is present.

KEYWORDS: Ir-catalyst; chlorine poisoning; gas–solid reaction; calcium oxide.

1. Introduction

It has been shown in our previous studies [1,2] that with platinum group metals (Pt, Pd, Ir, Rh) present the hydrogenation of solid $CaCO_3$ takes place via a specific pathway by which methane can be formed with the transformation of $CaCO_3$ into CaO at temperatures as low as 573 K and also the reverse reaction represented by the following equation proceeds.

$$CaO + CH_4 + 2H_2O \rightarrow CaCO3 + 4H_2 \qquad (1)$$

Ir and Rh were found to be superior catalysts for this gas–solid reaction. The use of CaO samples on which the metal catalysts were supported enabled us to obtain reproducible rate data, but the mechanism is not yet established partly because of a large difference in kinetic behavior between Ir/CaO and Rh/CaO samples used. Ir-catalyzed reactions carried out with the former sample which was prepared from commercially available catalyst of $Ir/CaCO_3$ showed an anomalous progress characterized by abrupt acceleration after initial linear progress to a certain extent (figure 1), contrary to the reaction with Rh/CaO prepared from precipitated catalyst of $Rh/CaCO_3$. Such the difference may arise from the difference in surface properties of the samples. One can easily suppose that residual chlorine originating from catalyst preparation might be responsible for the anomalous behavior of Ir/CaO, since platinum group metals are commonly impregnated on supports using chlorine-containing salts and a part of the chlorine often remains to act as poison for catalytic reactions, such as the oxidation of CO and hydrocarbons [3, 4, 5]. Very little information, however, is available in the literature about residual chlorine on Ir catalyst, especially on $Ir/CaCO_3$ and Ir/CaO, and also its effect on reactions other than the oxidation.

In the present work, therefore, the effect of residual chlorine on reaction (1) has been studied in relation to the anomalous progress mentioned above, using solid samples of Ir/CaO with different chlorine contents. The results are compared with those obtained in a similar study of methane steam reforming over $Ir/CaCO_3$ to get information on the reaction pathway taken when metal catalysts are supported on the reactant CaO.

2. Experimental

In order to obtain reproducible rate data, Iridium catalyst was supported on the reactant, CaO. Solid samples in this form, Ir/CaO, were prepared by the temperature-programed reduction (TPR) of $Ir/CaCO_3$ before use. In addition to a commercially available catalyst of 5% $Ir/CaCO_3$ (Johnson Matthey) previously used, similar catalysts were prepared by impregnation and precipitation methods using an aqueous solution of $IrCl_4$ (Wako Pure Chem.). In the former method, the solution was evaporated at 333 K, while in the latter Ir was precipitated on $CaCO_3$ by adding a solution of sodium tetra-hydroborate before filtration. Catalysts thus obtained were dried at 383 K overnight, calcined at 773 K for 5 h, and then reduced with flowing H_2 at 473 K for 1 h. TPR of these catalysts was carried out under flowing H_2 at 3 K/min up to 863 K. Weight-loss

---

*To whom correspondence should be addressed.

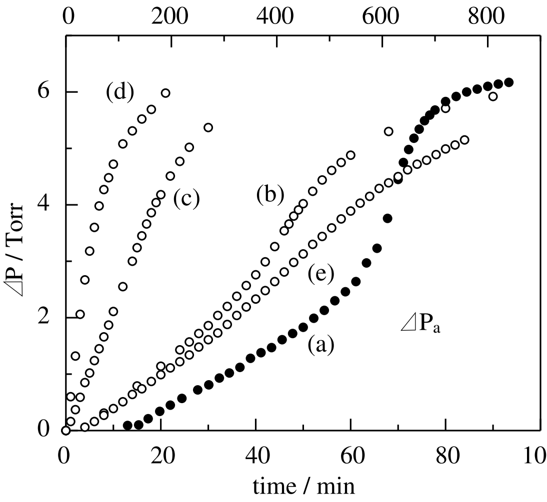

Figure 1. Pressure change against time curves for Ir-catalyzed reaction of 7.9 mg of CaO with 23 Torr of an equimolar gas mixture of CH_4 and H_2O: the reaction was carried out with: (a) Ir/CaO (Imp) at 713 K; (b) Ir/CaO (C) at 683 K; (c) Ir/CaO (P) at 683 K; (d) Ir/CaO (I-W) at 683 K; (e) Ir/CaO (I-W) at 633 K.

measurements with a Cahn electrobalance and XRD analysis confirmed almost complete transformation ($\geq 98\%$) of the carbonate into CaO.

Iridium and Chlorine contents were measured by atomic absorption analysis. MgKα radiation of 1253.6 eV was employed in XPS analysis (Kratos XSAM-800), in which carbon 1s impurity line at 284.6 eV was used for binding energy calibration [6]. BET area was determined by volumetric adsorption of Kr or N_2 at 77 K. Ir dispersion was determined by O_2 chemisorption at 300 K and also by subsequent titration with H_2, by assuming adsorption stoichiometries of H/Ir and O/Ir equal to unity. Isothermal kinetic runs were carried out in a closed circulation apparatus (275 mL) equipped with a Baratron capacitance manometer and a sampling tube for GC analysis (Yanaco G2800). Each run was initiated by admitting usually about 23 Torr of a 1 : 1 gas mixture of CH_4 and H_2O onto a Ir/CaO sample (CaO : 7.9 mg) preliminarily treated with 20 Torr of H_2 at a reaction temperature (613—713 K) for 30 min, and followed by manometric measurements. Steam reforming of methane was also carried out under similar conditions on Ir/$CaCO_3$, for comparison. In this case, H_2-pretreatment of the catalyst was performed at 473 K to avoid the chemical change of the support, $CaCO_3$. All the gases of more than 99.99% purity (Takachiho Chem.) were used as supplied.

3. Results and discussion

3.1. Surface properties

The main characteristics of Ir/$CaCO_3$ and Ir/CaO used here are summarized in table 1, in which commercially available catalyst of Ir/$CaCO_3$ is denoted by (C), in order to discriminate it against impregnated (Imp) and precipitated (P) catalysts and Ir/$CaCO_3$ (I-W) obtained by washing the impregnated catalyst in deionized water. The same symbols are given to the corresponding reduced samples, Ir/CaO.

Ir/$CaCO_3$ (P) contains only traces of chlorine and hence can be considered as free from chlorine, while Ir/$CaCO_3$ (Imp) contains 1.1% of chlorine which corresponds to about one-third the quantity of chlorine arising from the precursor, $IrCl_4$. It is noteworthy that a large portion of residual chlorine on Ir/$CaCO_3$ (Imp) can be washed away with water (Compare with Ir/$CaCO_3$ (I-W)). The amount of chlorine thus removed depended hardly on temperature, at least in the range 300–353 K. Thus, the removable chlorine is considered to exist as water-soluble species on the exposed surfaces of both metal and support, while the rest on other places such as subsurface of the support and metal-support interface including their boundaries. The presence of chlorine on metal surfaces is shown by the difference in Ir-dispersion between Ir/$CaCO_3$ (Imp) and Ir/$CaCO_3$ (I-W). The same would be the case for Ir/$CaCO_3$ (C). It is also shown in the table that some chlorine is lost in the TPR process. This and the water-soluble character mentioned above suggest that residual chlorine may be associated with Ca^{2+} ions to form $CaCl_2$, the melting point of which is low enough to permit vaporization during TPR. The binding energy of Ir $4f_{7/2}$ line was determined to evaluate the interaction with chlorine. The results obtained are as follows:

$$\text{Ir/CaCO}_3\text{(Imp); 61.0 eV,}$$

$$\text{Ir/CaO (C): 60.6 eV,} \quad \text{Ir/CaO (Imp) : 60.4 eV,}$$
$$\text{Ir/CaO (I-W): 60.6 eV.}$$

Although shifting from 61.0 eV for Ir/$CaCO_3$ (Imp) to 60.4 eV for its reduced sample, the binding energies are fairly close to the value (60.8 eV) reported for metallic Ir [7] and appreciably lower than those for IrClx [8]. This shows clearly that chlorine is not associated directly with Ir, in accord with the above discussion.

Table 1
Main characteristics of Ir/CaCO3 and Ir/CaO

Sample	BET-area (m^2/g)	Ir-loading (%)	Ir-dispersion	Cl-Content (%)
Ir/$CaCO_3$(C)	8.3	5.2	0.40	0.26
Ir/$CaCO_3$(Imp)	8.9	4.8	0.41	1.10
Ir/$CaCO_3$(I-W)	9.2	-	0.55	0.17
Ir/$CaCO_3$(P)	7.8	6.2	0.28	< 0.05
Ir/CaO(C)	15.7	(8.9)[a]	0.11	0.21
Ir/CaO(Imp)	9.2	(8.3)[a]	0.05	1.02
Ir/CaO(I-W)	26.3	-	0.19	0.17
Ir/CaO(P)	26.0	(10.6)[a]	0.15	< 0.05

[a] Calculated values by assuming 100% transformation of CaCO3 to CaO.

It is also interesting to note that in all cases studied the TPR process causes a significant decrease in Ir-dispersion. Possible explanations of this change include both an intrinsic change in exposed metal area due to sintering and apparent changes due to the adsorption of residual chlorine and a sinking of Ir particles into the bulk of CaO. The migration of chlorine from support to Ir at high temperatures might be reflected by the result that Ir/$CaCO_3$ (Imp) with higher chlorine content reveals a larger decrease in dispersion after TPR than Ir/$CaCO_3$ (I-W). Similar results were already reported by Roth *et al.* [4] and Gracia *et al.* [5], who explained the inhibiting effect of residual chlorine on the activity of Pt/Al_2O_3 by its surface migration during pretreatment with H_2 or calcination at high temperatures above 773 K. On the other hand, the clear difference in dispersion between chlorine-free Ir/$CaCO_3$ (P) and Ir/CaO (P) could be ascribed to other causes, such as a sinking and sintering of Ir particles.

3.2. Kinetic results of reaction (1)

Figure 1 shows typical reaction curves obtained with the four samples of Ir/CaO. Hydrogen was selectively formed in all runs shown.

It can be seen that Ir/CaO (Imp) with the highest chlorine content exhibits the lowest reactivity towards the gas mixture and the longest induction period. This indicates an inhibiting role of chlorine, which is confirmed undoubtedly by an extremely large difference in rate between the reactions with Ir/CaO (I-W) and Ir/CaO (Imp). The former sample exhibits more than 300 times higher reactivity than the latter, which is much larger than would be expected from their Ir-dispersion. It should also be noted that the reactions with chlorine-containing samples of Ir/CaO (C), Ir/CaO (Imp) and Ir/CaO (I-W) are accelerated abruptly after the initial linear progress to a certain extent of conversion ($\Delta p =$ 2–3 Torr) to reveal distinct two stages, but not the reaction with a chlorine-free sample of Ir/CaO (P). Despite such a difference in reaction progress, the kinetics appears to be independent of chlorine contents, since apparent activation energy of 177 kJ/mol and reaction order of 1.0 with respect to CH_4 pressure are determined for Ir/CaO (C), while the energy of 186 kJ/mol and the order of 0.8 for Ir/CaO (P). These findings lead us to conclude that residual chlorine does not affect the route of reaction (1) but the rate. At the end of all runs shown in figure 1, some fraction of CaO remains unaltered, since 11.5 Torr of water vapor in the mixture is equivalent to nearly one-half of the amount required to transform 7.9 mg of the CaO used (1.4×10^{-4} mol). Then, the reaction was continued until the solid reactant was completely converted to $CaCO_3$ by repeated introduction of the standard gas mixture (23 Torr) after evacuation for 30 min. figure 2 shows the result of four successive runs carried out with one sample of Ir/CaO (C) at 673 K.

The third and fourth runs reveal normal or simple reaction curves, contrary to the preceding two runs. This and the detection of CO and CO_2 from the beginning indicate the occurrence of methane steam reforming probably due to the completion of the transformation of CaO into $CaCO_3$ in the first and second runs, in accord with what would be expected from a material balance. It appears strange that the abrupt acceleration is again observed in the second run. This can be explained, however, by assuming that solid surfaces is restored during the evacuation to nearly the same state of CaO as in the beginning of the first run. These considerations lead us to conclude that the acceleration phenomenon might be related to the formation of $CaCO_3$. Another explanation by a progressive increase of catalytically active sites on the metal surface due to the formation of H_2 can be excluded in our case, since 5–20 Torr of H_2 added to a starting gas mixture was found to have no effect on the rate of reaction (1). This was checked by determining Ir-dispersion during the reaction, which was carried out by repeated admission of the standard gas mixture onto 41 mg of Ir/CaO (C). The result obtained (table 2) demonstrates that Ir area does not increase but rather decrease gradually with the progress of the reaction, in accord with the above conclusion.

The observed decrease might be ascribed mainly to a sinking of Ir particles, since the dispersion once lowered does not recover to the initial even after TPR.

3.3. Mechanism of acceleration

Methane steam reforming on Ir/$CaCO_3$ was studied at 633 K, as a limiting model of reaction (1). figure 3 shows pressure change against time curves for Ir/$CaCO_3$ (Imp) and Ir/$CaCO_3$ (I-W).

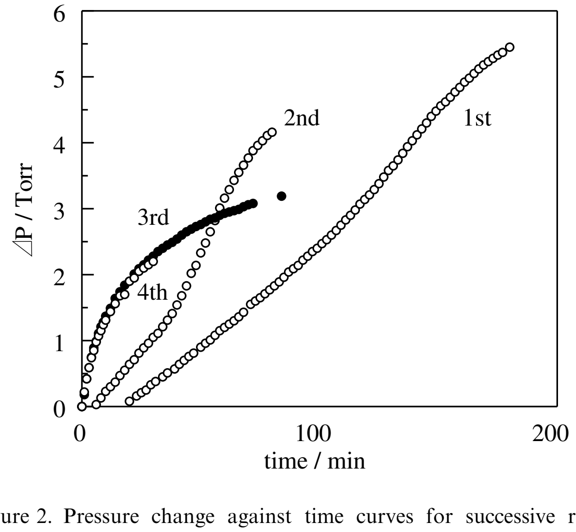

Figure 2. Pressure change against time curves for successive runs carried out at 673 K by repeated introduction of equimolar gas mixtures [23 Torr: $CH_4 = H_2O = 1.7 \times 10^{-4}$ mol] onto a sample of Ir/CaO(C) containing 7.9 mg of CaO [1.4×10^{-4} mol].

In both cases, CO/CO_2 and H_2/CO_2 ratios were determined to be 0.10 and 4.0 at $\Delta P = 3.0$ Torr,

Table 2
Variation of Ir-dispersion during reaction (1)

Conv. of CaO (%)	0	15	38	75	100	After TPD
Ir-dispersion	0.12	0.10	0.08	0.06	0.05	0.08

respectively. Thus, the overall process can be represented roughly by $CH_4 + 2H_2O \rightarrow 4H_2 + CO_2$, in accord with thermodynamic prediction. The kinetics of the reforming processes over $Ir/CaCO_3$ (C) and $Ir/CaCO_3$ (Imp) were found to be the same, i.e., slightly negative order with respect to CH_4 (not determined precisely) and apparent activation energy of 102 kJ/mol, both of which are entirely different from those for reaction (1). It is interesting that lowering of chlorine content from 1.1% to 0.2% results in rate-enhancement by only a factor of 1.5, which is nearly identical to the ratio of Ir dispersions. Turnover numbers (TON) of CH_4 were calculated to be as follows:

$$Ir/CaCO_3(Imp) : TON = 0.78[molec./metal\text{-}sites]$$

$$Ir/CaCO_3(I\text{-}W) : TON = 0.89[molec./metal\text{-}sites]$$

Good agreement shows clearly that the steam reforming involves only metal sites. This provides an insight into reaction (1), which is influenced significantly by residual chlorine. The fact that the difference in rate between the reactions with Ir/CaO (Imp) and Ir/CaO (I-W) is much larger than expected from Ir dispersion indicates that Ir-catalyzed steam reforming to form H_2 and CO_2 is not involved as a rate-determining step. The interaction of CaO with CO_2 may not also be rate-determining, since CaO is known to react so rapidly with CO_2. Actually, at 683 K all of the samples of Ir/CaO studied here showed instantaneous uptake of CO_2 at least up to nearly 70% conversion of CaO, regardless of the presence of water vapor. Consequently, the consecutive mechanism of methane steam reforming followed by CO_2 absorption can be entirely ruled out. This is supported by a considerable difference in kinetic parameters between reaction (1) and methane steam reforming over $Ir/CaCO_3$. Thus, we feel the mechanism previously discussed [2] to be plausible, in which CH_X species activated on Ir are proposed to interact with OH species activated on CaO. Negative order previously determined with respect to water vapor can be explained by assuming spillover of OH species on CaO to the metal surface, according to the concept of Rostrup-Nielsen [9]. It must be also the spiltover OH species that severely hinder the steam reforming of methane on Ir.

Finally, the correlation of the acceleration phenomenon with the formation of $CaCO_3$ is briefly discussed. The result of CaO–CO_2 interaction mentioned above shows clearly that the carbonate layer acting as a barrier to the diffusion of CO_2 would not be formed below about 70% conversion of CaO. On the other hand, acceleration point (ΔP_a) was found to vary with starting gas compositions [2]. In the reaction with Ir/CaO (C) containing 7.9 mg of CaO, for example, 34.2 Torr of a 1 : 2 gas mixture of CH_4 and H_2O showed no acceleration up to the end point (about 60% conversion of CaO), while 57.0 Torr of a 4 : 1 mixture showed $\Delta Pa = 0.6$ Torr (about 6% conversion of CaO). Thus, it is evident that the formation of rigid $CaCO_3$ layer is not required for the acceleration of reaction (1). It has been recognized, however, that gas–solid reactions take place through the nucleation which involves conversion of a small volume of reactant into a stable particle of product and their growth [10]. This suggests the importance of $CaCO_3$ particles transiently formed on the surface, from which the following mechanism can be derived: Residual chlorine blocks nucleation sites near the boundaries between Ir particles and CaO to exert inhibiting effect. This effect is emphasized by the presence of water vapor, but improved by a change in the reaction atmosphere; e.g., a decrease in H_2O vapor pressure and increase in CH_4/H_2O ratio. Such the favorable change in surface properties results in the acceleration phenomenon. According to this mechanism, the fast progress without any acceleration in the reaction with a chlorine-free sample of Ir/CaO can be explained by the instantaneous formation of many nuclei and their steady growth.

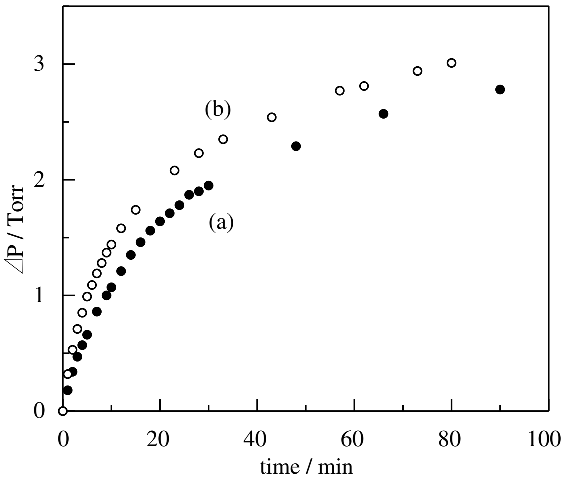

Figure 3. Pressure change against time curves at 633 K for methane steam reforming initiated by admitting 23 Torr of an equimolar gas mixture of CH_4 and H_2O onto 14.8 mg of (a) $Ir/CaCO_3$ (Imp) and (b) $Ir/CaCO_3$ (I-W).

Further detailed studies from both kinetic and spectroscopic points of view are now in progress, to elucidate the mechanism of reaction (1).

References

[1] N. Yoshida, T. Hattori, E. Komai and T. Wada, Catal. Lett. 58 (1999) 119.

[2] N. Chikazawa, Y. Fujisaki, Y. Sato, M. Suehiro and N. Yoshida, Catal. Lett. 77 (2001) 63.

[3] D.O. Simone, T. Kenelly, N.L. Brungard and R.J. Farrauto, Appl. Catal. 70 (1991) 87; E. Marceau, M. Che, J. Saint-Just and J.M. Tatibauet, Catal. Today 29 (1996) 415.
[4] D. Roth, P. Gelin, M. Primet and E. Tena, Appl. Catal. A 203 (2003) 37.
[5] F.J. Gracia, J.T. Miller, A.J. Kropf and E.E. Wolf, J. Catal. 209 (2002) 341.
[6] G. Johansson, J. Hedman, A. Brendtsson, M. Klasson and R. Nilsson, J. Electron Spectroc. 2 (1973) 295.
[7] T.S. Marinova and K.L. Kostov, Surf. Sci. 181 (1987) 573.
[8] B.D. El-Issa, A. Katrib, R. Ghodstan, B.A. Salsa and S.H. Addassi, Int. J. Quantum Chem. 33 (1988) 195; B. Folkesson, Acta Chem. Scand. 27 (1973) 287.
[9] J.R. Rostrup-Nielsen and J. Sehested, Adv. Catal. 47 (2002) 65.
[10] Y. Koga and L.G. Harrison, m:Comprehensive Chemical Kinetics, vol.21,eds. C.H.
[11] Bamford, C.H.F. Tipper and R.G. Compton (Elsevier, Amsterdam, 1984) ch.2.