

Materials Research for Hydrogen Generation by Thermochemical Cycles

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**Over the past century,
From wood fuel to coal, then to oil
and now to natural gas.**

**Slow reduction in the amount of carbon
An increase in its hydrogen content.**

Total elimination of carbon and use pure hydrogen.

Future hydrogen economy

Fuel cells for vehicles

Supply of electricity with the help of micropower plants.

**The greatest advantage of hydrogen in electrochemical
fuel cells is that it creates no harmful emissions, the
only by-product being water.**

Today hydrogen is mainly produced from fossil resources.

In the long term, because of

increasing energy demand,

lack of fossil resources

and limitations on the release of green house gases,

only water and biomass are viable, long term candidate raw materials for hydrogen production.

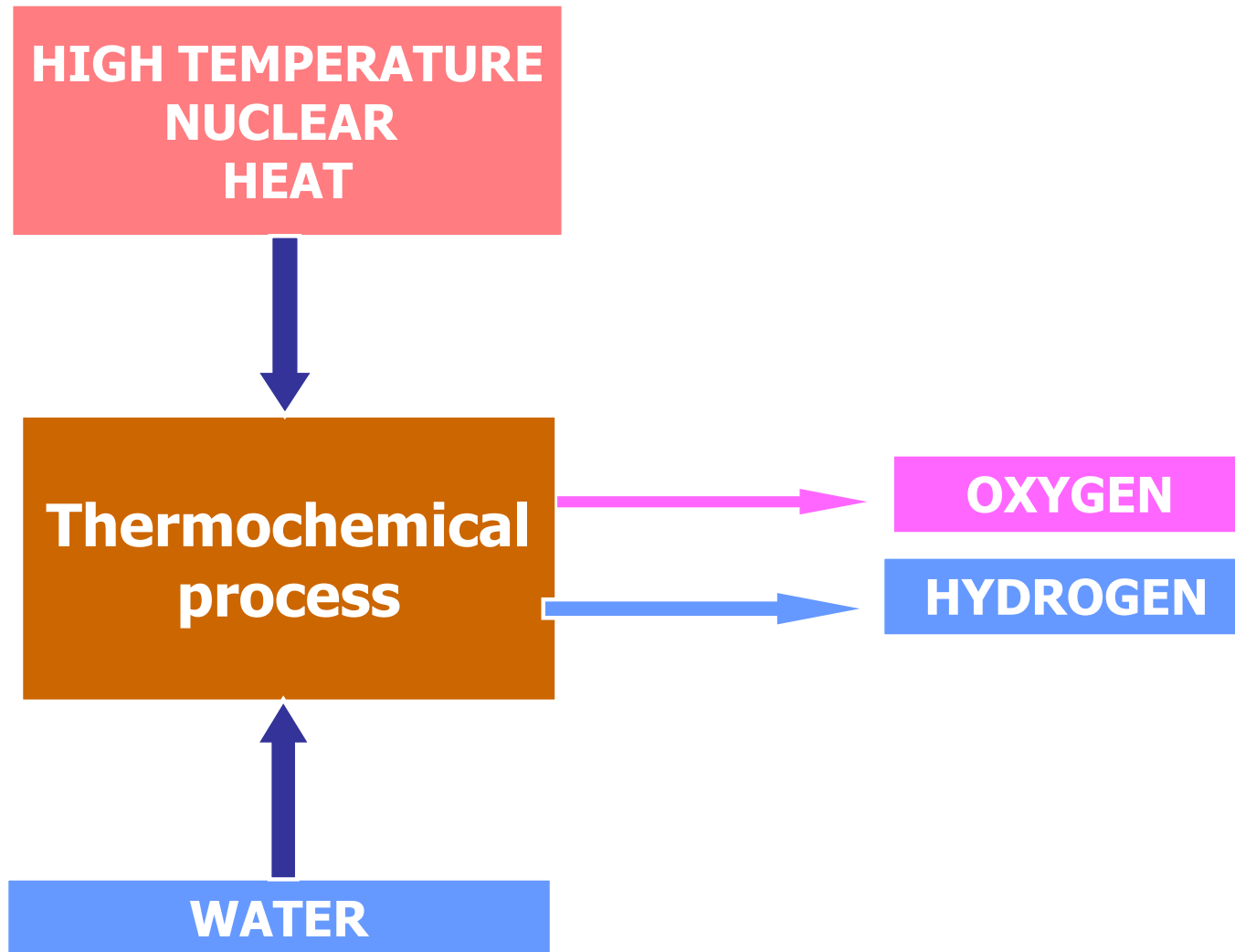
The two processes that have the greatest likelihood of successful massive hydrogen production from water are electrolysis and thermochemical cycles.

As heat can be directly used in thermochemical cycles, they have the potential of better efficiency than alkaline electrolysis.

The required energy can be provided by nuclear reactor.

Thermochemical Process

Split water to obtain hydrogen by utilising nuclear heat (HTGR).



A large number of thermochemical cycles have been tested

Some of these cycles have been demonstrated

We will consider a few of the most promising cycles

The sulphur – iodine cycle will be discussed in more details

Countries currently advancing nuclear technology for Hydrogen Production

Sulphur – Iodine Thermochemical Cycle

General Atomics (USA)

Sandia National Laboratory (USA)

Commissariat à l'Énergie Atomique (CEA) (France)

Korean Atomic Energy Research Institute (Korea)

Japan Atomic Energy Agency (Japan)

(Aim – 60,000 m³/hr of hydrogen by 2020)

Copper – Chlorine Cycle

Atomic Energy of Canada Ltd. (Canada)

Steps in the Cu-Cl Thermochemical Cycle for Hydrogen Production

1. $2\text{Cu(s)} + 2\text{HCl(g)} = 2\text{CuCl(l)} + \text{H}_2\text{(g)}$ 430-475°C
2. $2\text{CuCl(s)} = 2\text{CuCl(aq)}$
3. $2\text{CuCl(aq)} = \text{CuCl}_2\text{(aq)} + \text{Cu(s)}$ Ambient temperature Electrolysis
4. $\text{CuCl}_2\text{(aq)} = \text{CuCl}_2\text{(s)}$ > 100°C
5. $2\text{CuCl}_2\text{(s)} + \text{H}_2\text{O(g)} = \text{CuO} \cdot \text{CuCl}_2\text{(s)} + 2\text{HCl}$ 400°C
6. $\text{CuO} \cdot \text{CuCl}_2\text{(s)} = 2\text{CuCl(l)} + 1/2 \text{O}_2\text{(g)}$ 500°C

The Cu-Cl cycle is well matched to Canada's Nuclear Reactors

Heat requirements adaptable to the Super Critical Water Reactor (SCWR)

SCWR – Canada's Generation IV Nuclear Reactor

Advantages:

Inexpensive chemical reagents

Reactions going to completion without side reactions

**Further data needed for better understanding
of the functionality of materials
with the working fluids in the Cu-Cl Cycle**

Thermal Behaviour

Mechanical stresses and fracture toughness

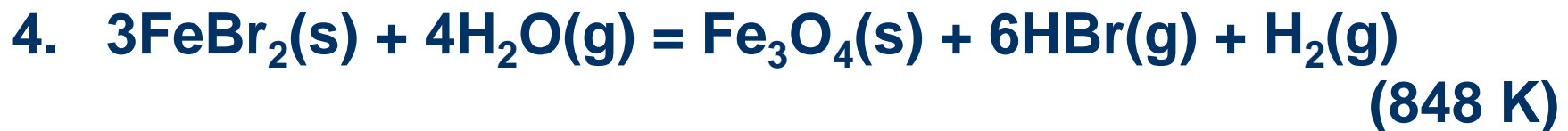
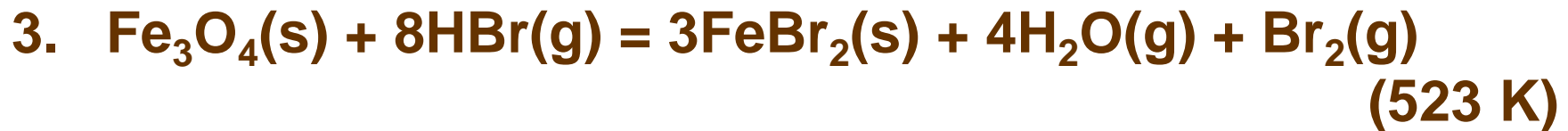
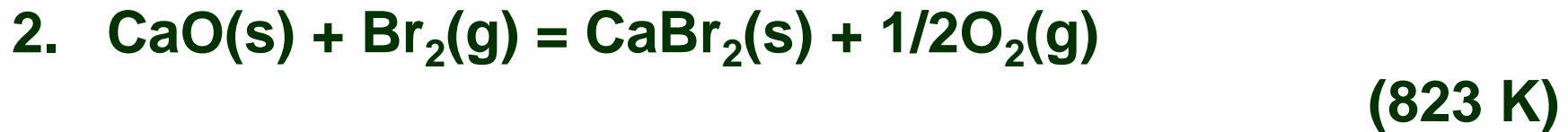
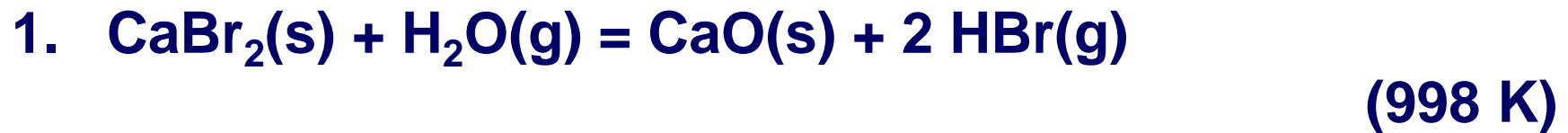
Strength and corrosion resistance over time

Materials Development for improved performance

**Work in India – Mumbai University Institute of
Chemical Technology**

The UT3 Cycle

Developed at the University of Tokyo during 1980-1990



The UT3 Cycle

Reactions 1 and 3 produce reactants for reactions 2 and 4

This cycling may cause coupling problems with a continuous heat source from a nuclear reactor because of variations in the temperature and heat demand for the four reactions.

There are difficulties because of sintering of solid reactants.

Other problems:

High cost of fabrication

Bromine toxicity

The Hybrid Sulphur Westinghouse Cycle



Electrolysis 30-90°C



Thermochemical 800-950°C

The main drawback is the use of an electrolytic step

Theoretical voltage = 0.17 V

Due to over potential, the cell voltage is 0.6 V

The Hybrid Sulphur Westinghouse Cycle

**Special caution to avoid sulphur or H₂S formation
In the electrolytic step**

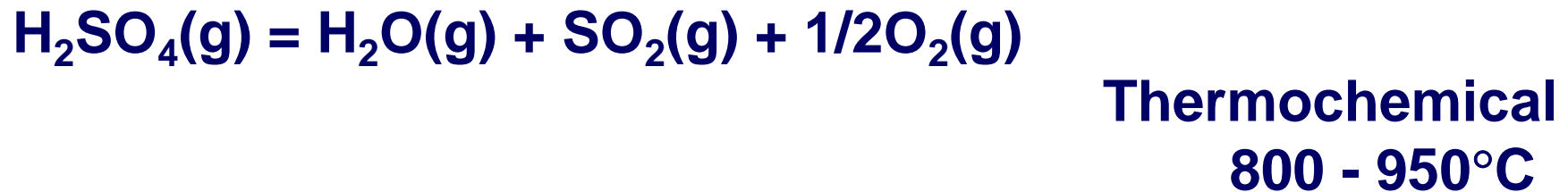
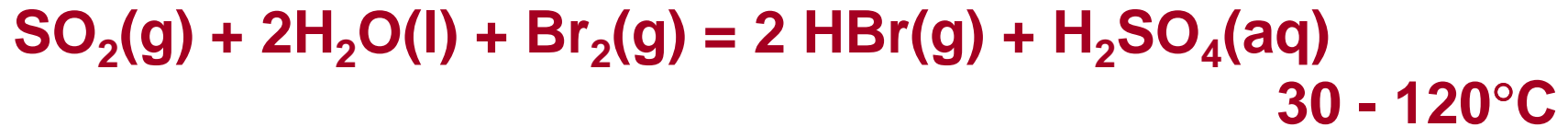
Advantages:

Only one chemical step

**Avoids problems of purity encountered
in other thermochemical cycles**

The calculated industrial efficiency 37 to 40 %

Hybrid Sulphur Bromine Ispra Cycle



Minimum H₂S and Sulphur formation

Less water is formed in H₂SO₄(aq)

(Compared to Hybrid S Cycle)

Hybrid Sulphur Bromine Ispra Cycle

Problems:

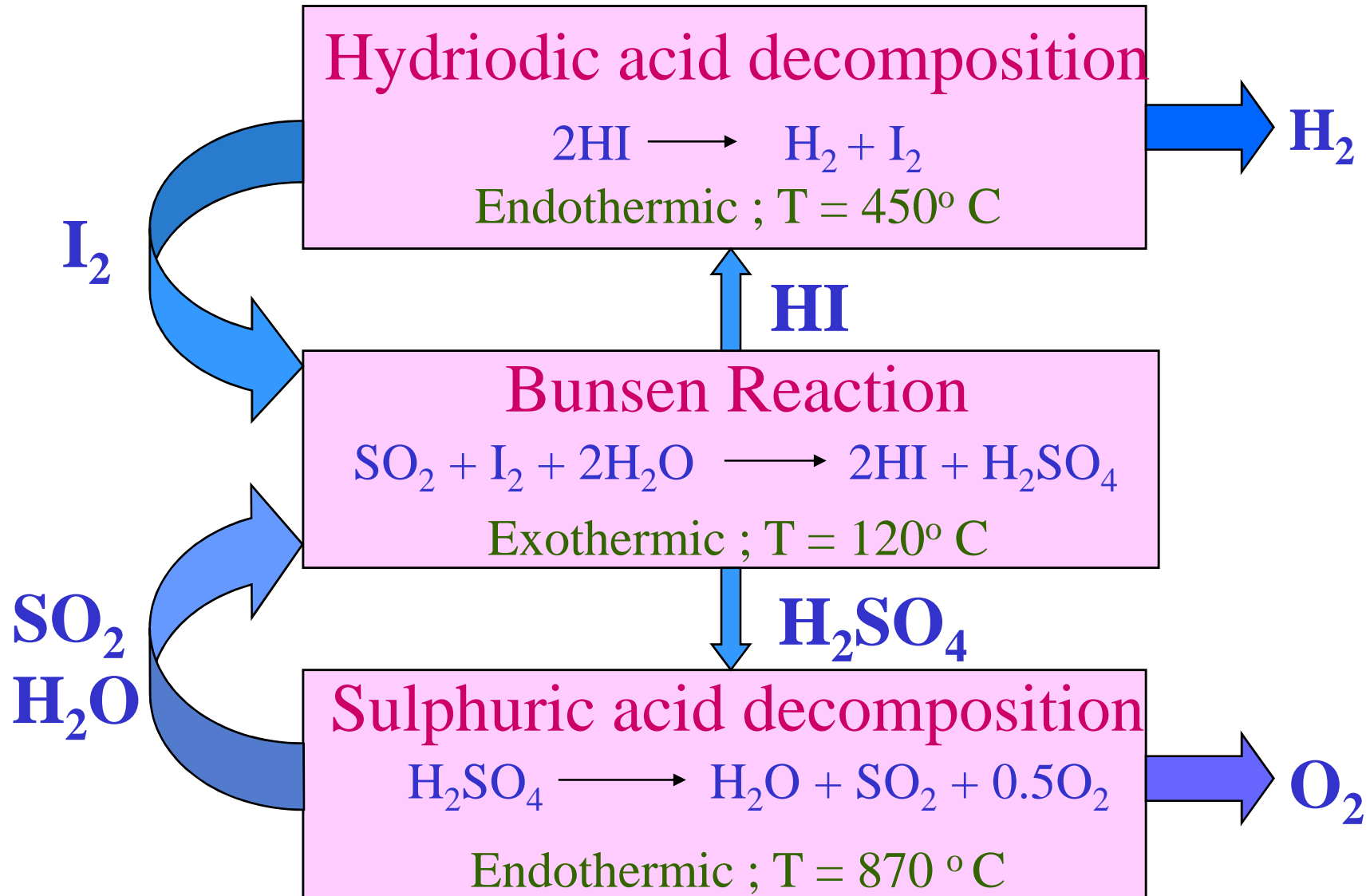
Voltage needed 1.066 V at ambient temperature

**Voltage can be considerably lowered
by operating at a higher temperature**

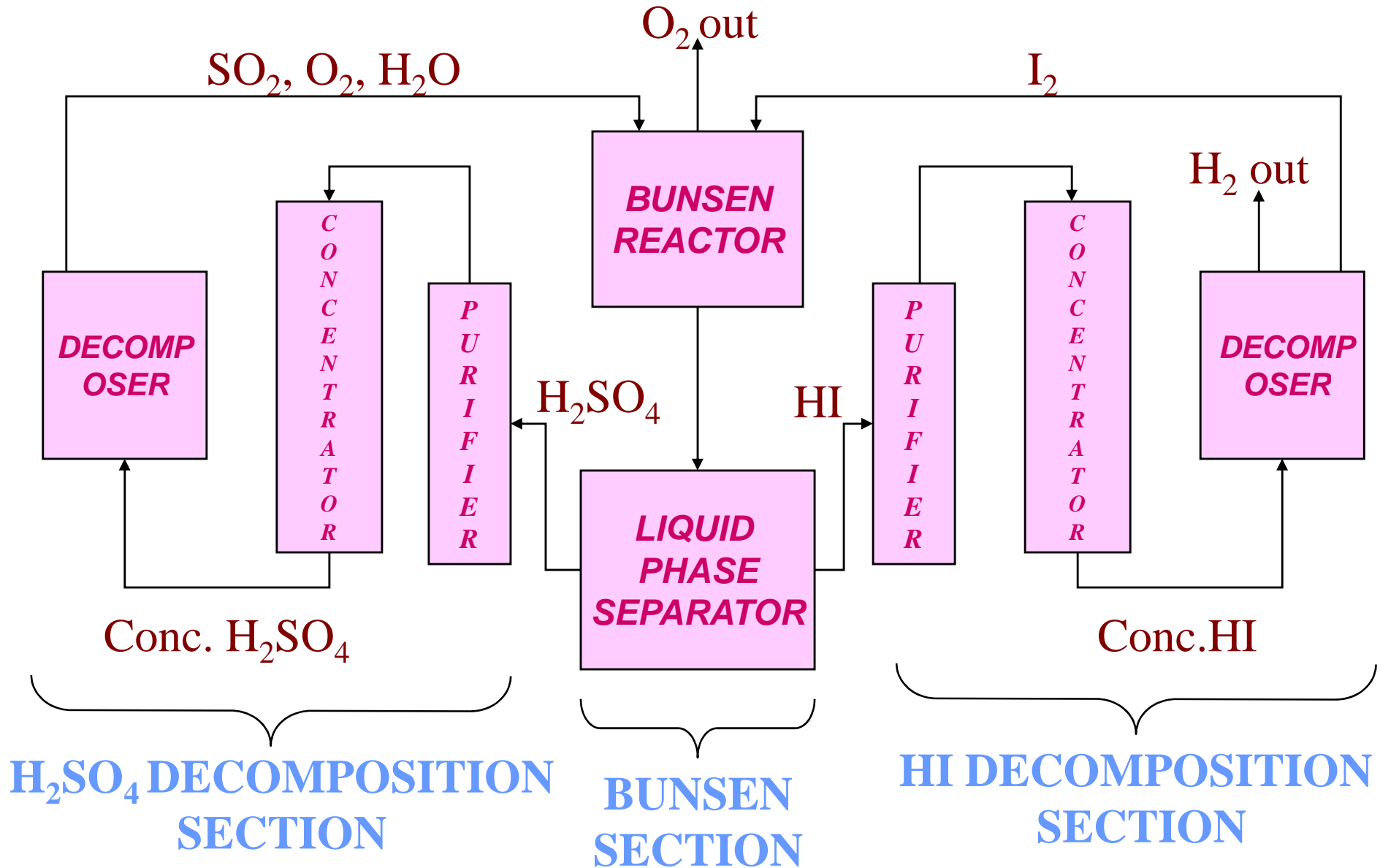
Ispra demonstration operated at 0.8 V

Another problem: Toxicity of Bromine

Iodine-Sulfur Thermochemical Process



Flow sheet of closed cycle H_2 production by Iodine-Sulfur process



How are we going about ?

- Lab scale experiments on H_2SO_4 and HI_x decomposition and Bunsen reaction
i.e. perform stand alone tests on component sections.
- Investigate process alternatives, materials, catalysts
Utilize improved materials, catalysts as available
- Integrate component sections and perform closed loop operation

The H₂SO₄ Decomposition

Distillation:



Evaporation:



Catalytic decomposition:



Sulphuric acid section

The main concern is about the high temperature step of the process, namely SO_3 into SO_2 decomposition.

This reaction, which requires a temperature in the 870°C range will take place in a reactor and use the heat from CHTR. This reactor will require a very high temperature heat exchanger, which will raise technological issues.

The temperature provided by CHTR is not high enough to avoid the use of catalyst for the reaction.

The long term resistance of this catalyst under the severe conditions that prevail will have to be ensured.

Platinum on porous metal oxides seems to be the most promising catalyst.

But, Pt catalysts are not stable in high temperature reaction environment.

Deactivation due to sintering of Pt and supports.

**As much as 30% of Pt lost in 10 day tests
(due to sintering and volatility)**

Research Directions

Increase Stability

Modify Pt sites with other PGMs

Explore supports with stronger metal/support interactions

Explore non-PGM catalysts

Spinel (AB_2O_4), Perovskites (ABO_3),
Mixed oxides

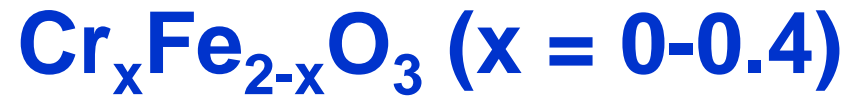
Catalysts reported to be active in temperature range 750°-950°C

1. *Dokiya et al.* $\text{Fe}_2\text{O}_3 > \text{V}_2\text{O}_5 > \text{Cr}_2\text{O}_3 > \text{CuO} > \text{TiO}_2 > \text{ZnO} > \text{NiO}$, $\text{MnO}_2 > \text{Al}_2\text{O}_3$ (1977)
2. *Brittain et al.* $\text{CuO} > \text{Cr}_2\text{O}_3 > \text{Fe}_2\text{O}_3 > \text{NiO}$ (1983)
3. *Tagawa et al.* $\text{Pt} \approx \text{Cr}_2\text{O}_3 > \text{Fe}_2\text{O}_3 > \text{CeO}_2 > \text{NiO} > \text{Al}_2\text{O}_3$ (1989)
4. Supported noble metal (Pt) – Highly active for this reaction.
Disadvantageous from the economic point of view & also suffers from deactivation due to sintering of Pt and supports.

Aim: synthesis of **multi-metal oxide** systems to fulfill the essential requirement of materials with better chemical, thermal stability and catalytic properties

V. Barbarossa et al. Fe_2O_3 & intermetallic alloy Ag–Pd, Italy.
T.-H. Kim et al. Fe/Al and Fe/Ti oxide catalysts, Republic of Korea.
D.M. Ginosar et al. Pt/ Al_2O_3 and Pt/ ZrO_2 USA.

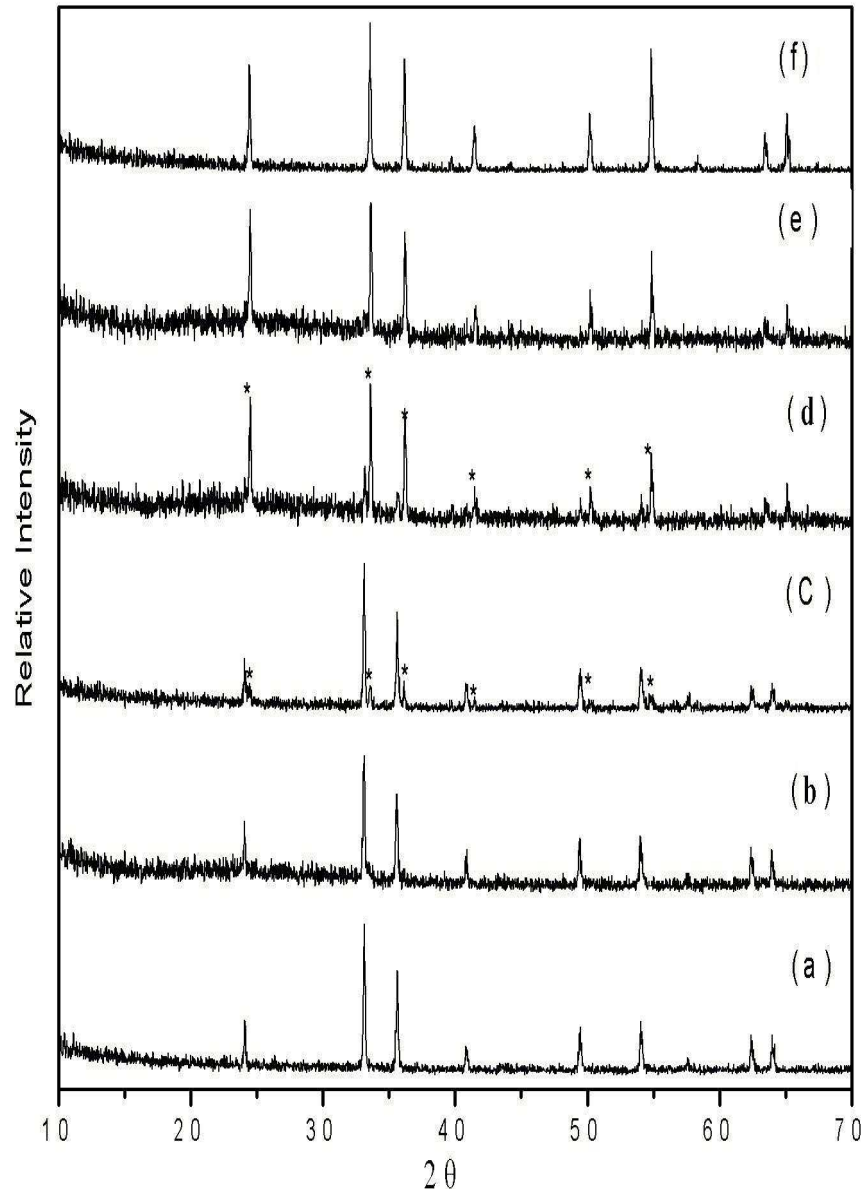
Catalyst systems investigated:



- ❖ Synthesis via Solid state route
- ❖ Characterization by XRD, IR
- ❖ Redox behavior by TPR/O
- ❖ Sulfuric acid decomposition: Quartz reactor, 2 g catalyst, H_2SO_4 (59 vol.% in N_2), 98 cc min^{-1}
- ❖ Product analysis: GC, IR, MS

Structural Analysis

XRD

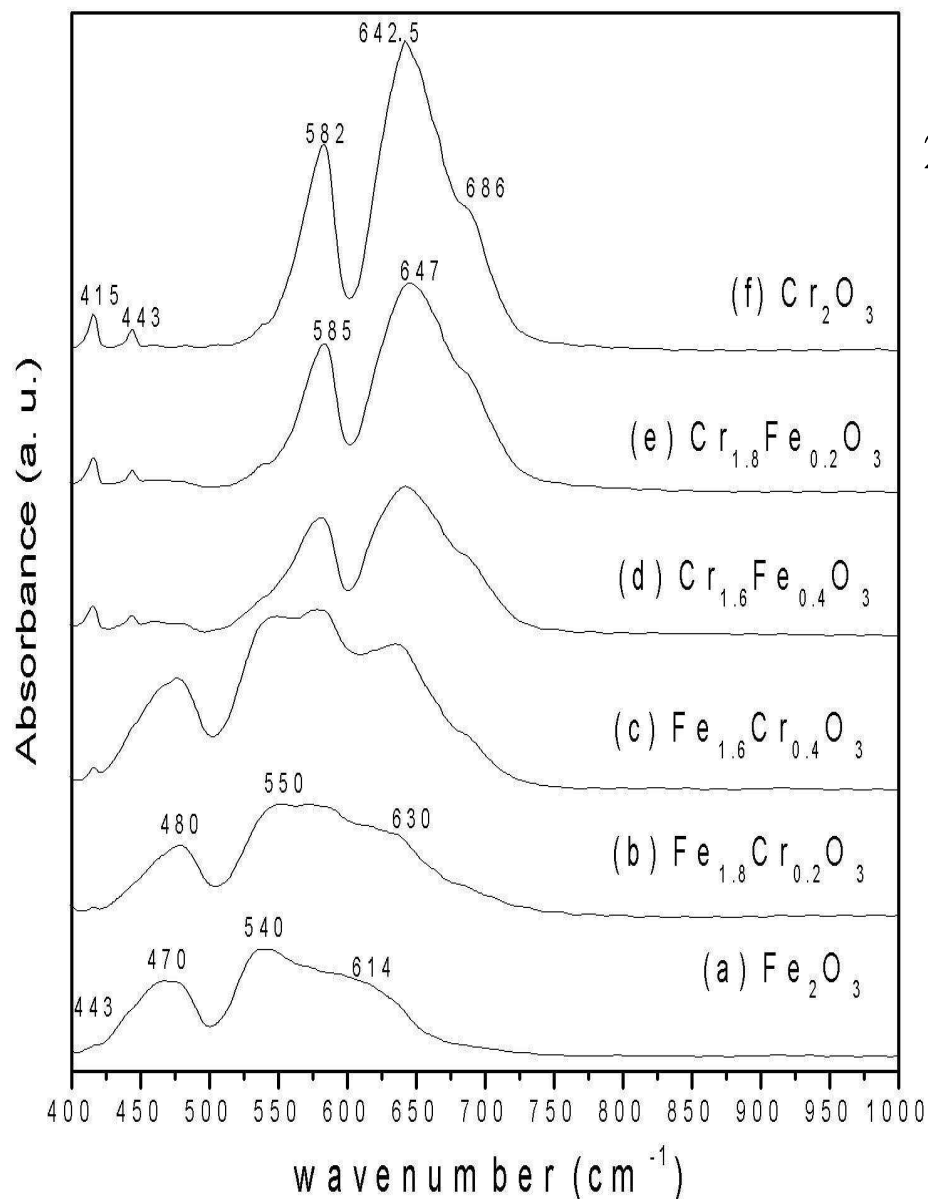


$2x =$ (a) 0, (b) 0.2, (c) 0.4, (d) 1.6, (e) 1.8 (f) 2.

* XRD lines due to Cr_2O_3 phase.

substituting either side upto 10%
results in formation of solid solutions

IR Spectra of the Oxides



$2x =$ (a) 0, (b) 0.2, (c) 0.4, (d) 1.6, (e) 1.8, (f) 2.

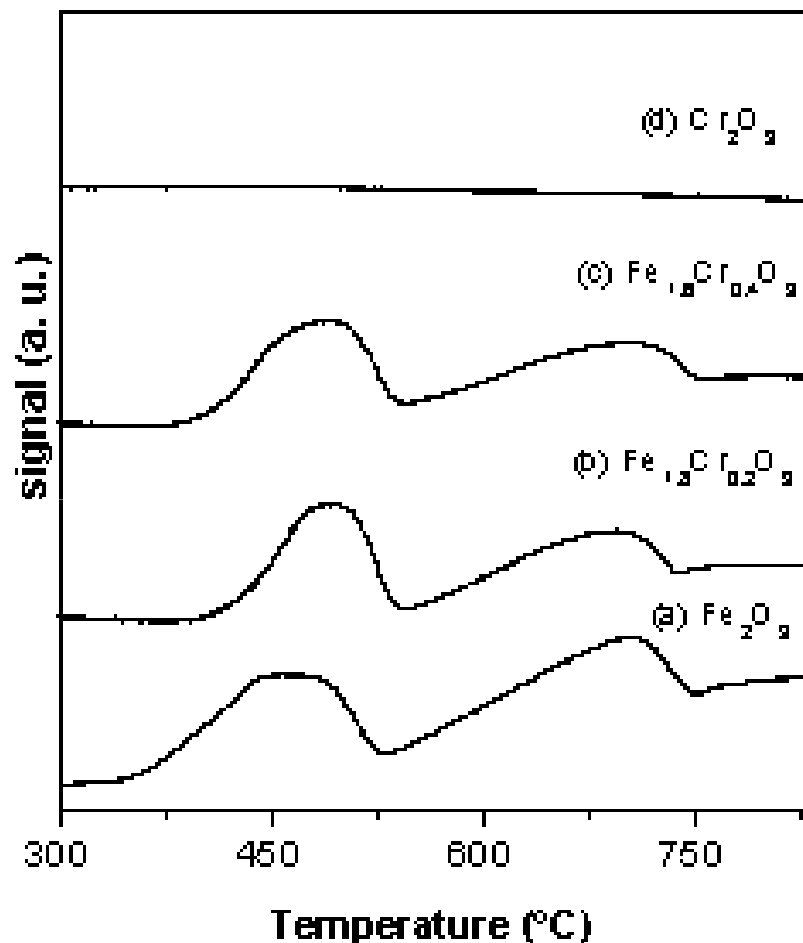
Fe_2O_3 - characteristic bands at 540, 470 and 345 cm^{-1}

Cr_2O_3 - characteristic bands at 415, 444, 582, 642 cm^{-1}

$\text{Fe}_{1.8}\text{Cr}_{0.2}\text{O}_3$ and $\text{Fe}_{0.2}\text{Cr}_{1.8}\text{O}_3$ bands exclusively due to Fe_2O_3 and Cr_2O_3 respectively

$\text{Fe}_{1.6}\text{Cr}_{0.4}\text{O}_3$ and $\text{Fe}_{0.4}\text{Cr}_{1.6}\text{O}_3$ spectral characteristics of both Fe_2O_3 and Cr_2O_3

TPR/O studies



Fe₂O₃ - onset of reduction 330°C

T_{max} ~ 470°C & 700°C

three reduction steps:

Fe₂O₃ to Fe₃O₄ at 400°C,

Fe₃O₄ to FeO at 600°C

FeO to Fe metal at 720°C

Cr₂O₃ – stable in H₂ atm upto 1000°C

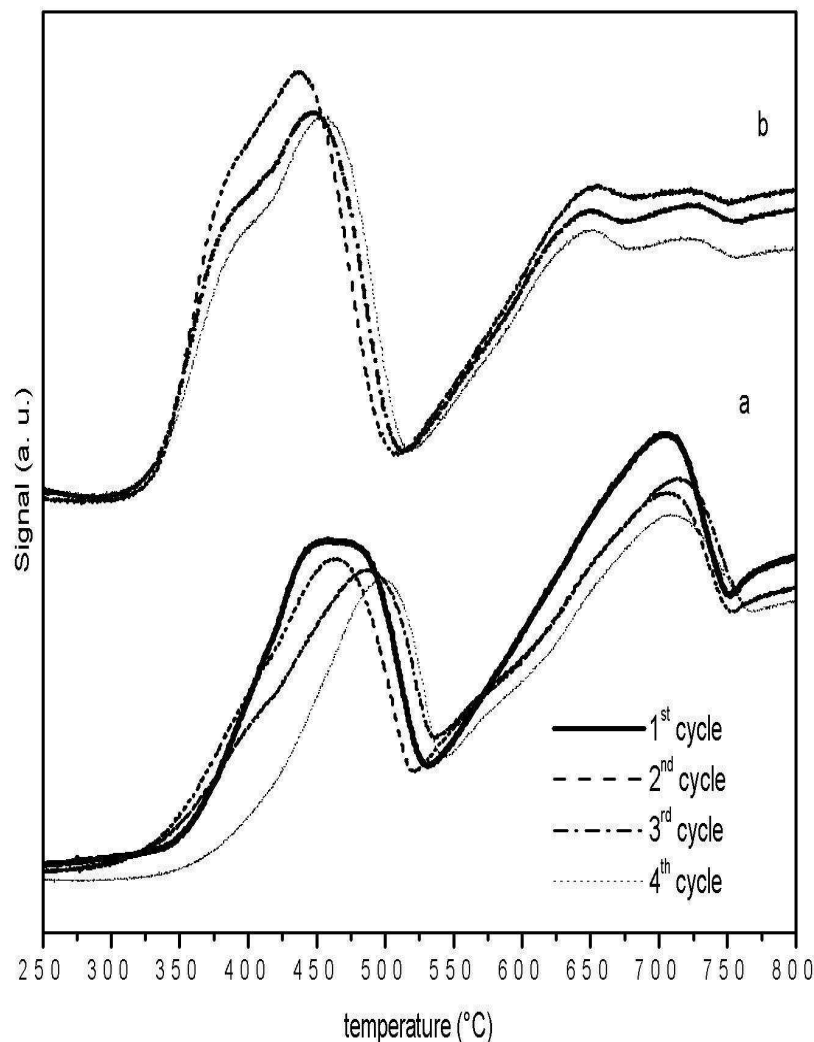
Tmax ~ 450-490°C

Less than Fe/Al and Fe/Ti oxides*.

Typical first TPR cycle of
substituted and unsubstituted samples

**T.-H. Kim et al. Applied Catalysis A: General 305 (2006) 39–45*

Successive TPR cycles



Fe₂O₃ - TPR profile shifts to a higher temperature range in subsequent cycles

Fe_{1.8}Cr_{0.2}O₃ - reproducible behavior towards repeated TPR cycles

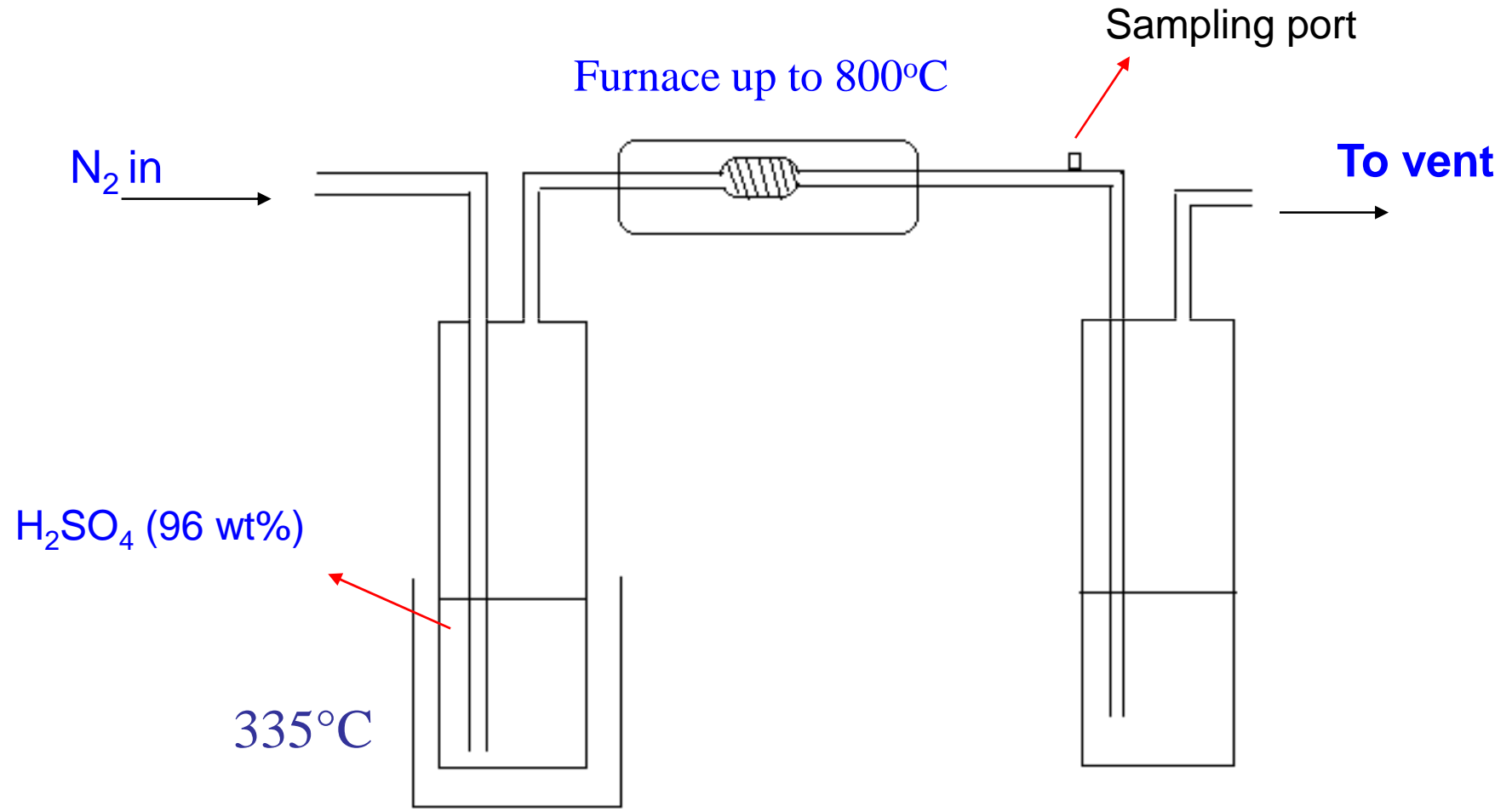
simple oxide catalysts faces the main drawback of sintering when subjected to repeated cycles of reduction and oxidation

Successive 4-5 TPR cycles of

(a) Fe₂O₃ (b) Fe_{1.8}Cr_{0.2}O₃.

Each TPR cycle is followed by a TPO run.

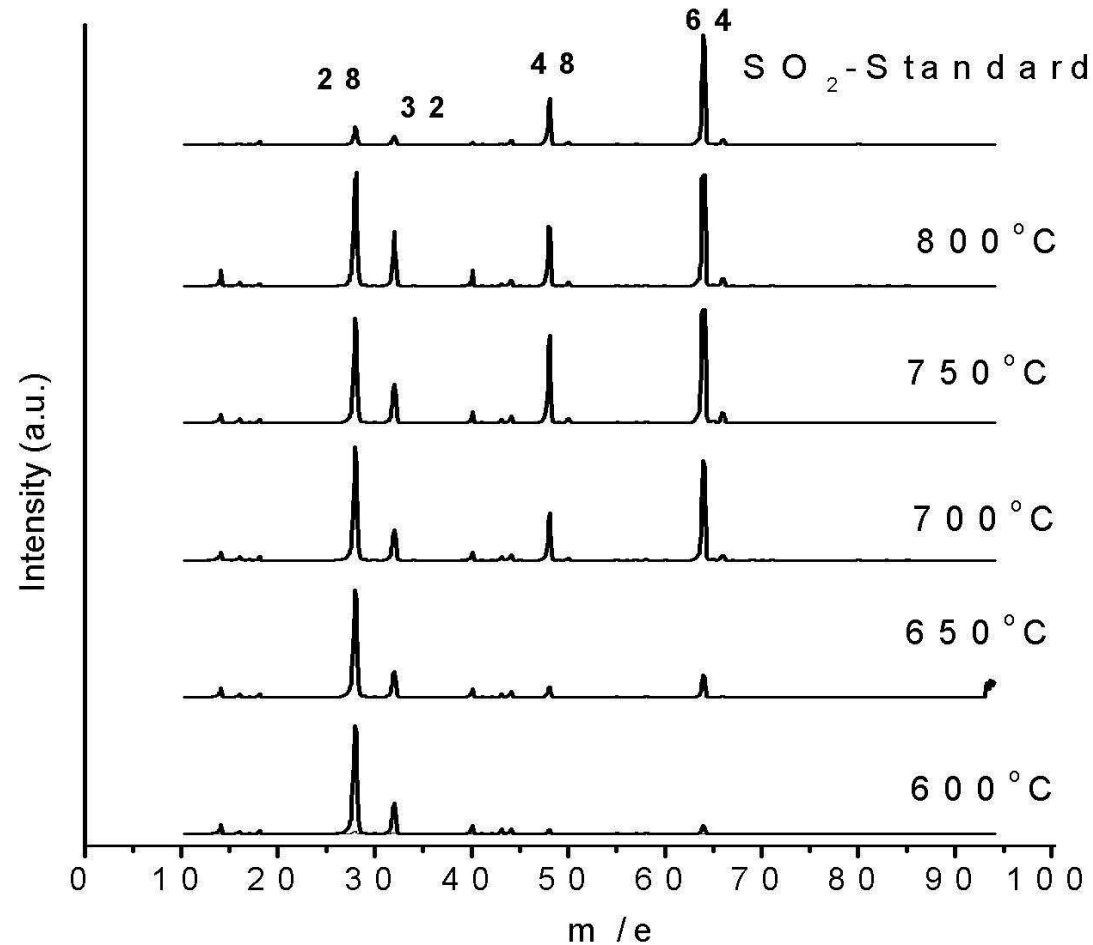
Block diagram of experimental set up used for sulfuric acid decomposition reaction



Glass Set-up for sulfuric acid decomposition

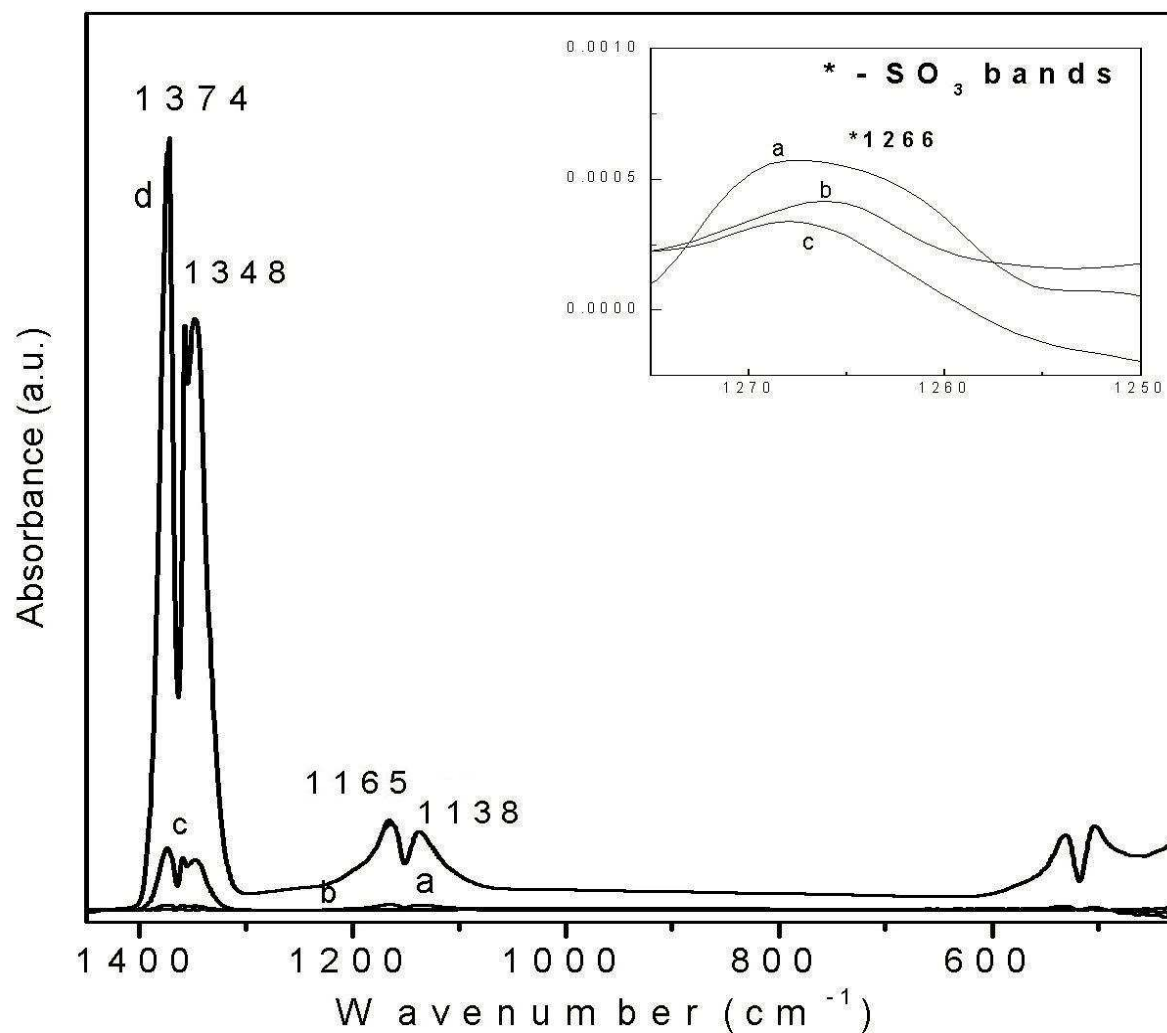


Catalytic activity



Identification of SO₂ in effluent gases of sulfuric acid decomposition reaction at different reaction temperatures by mass spectrometry.

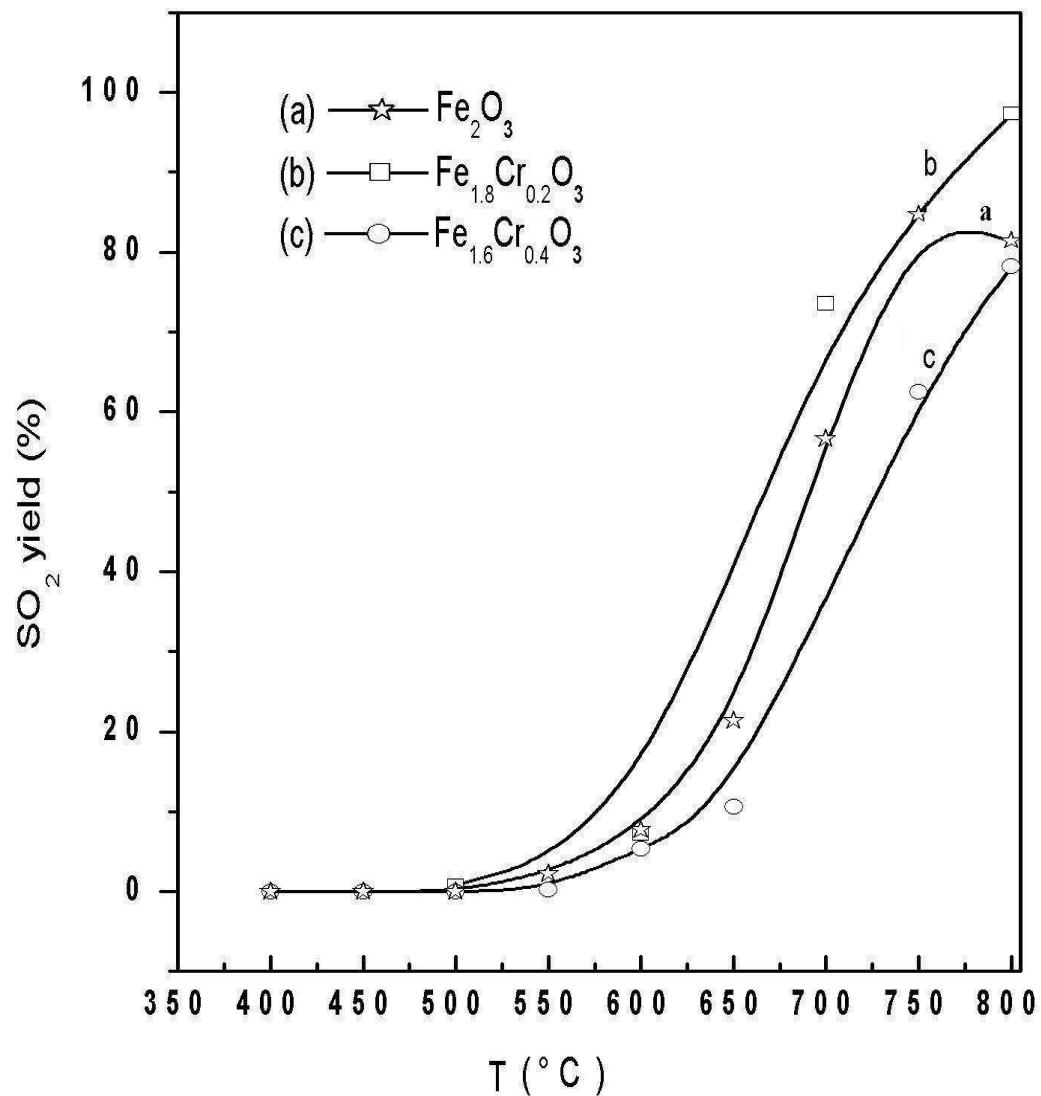
FTIR



- a 400°C
- b 500°C
- c 600°C
- d 800°C

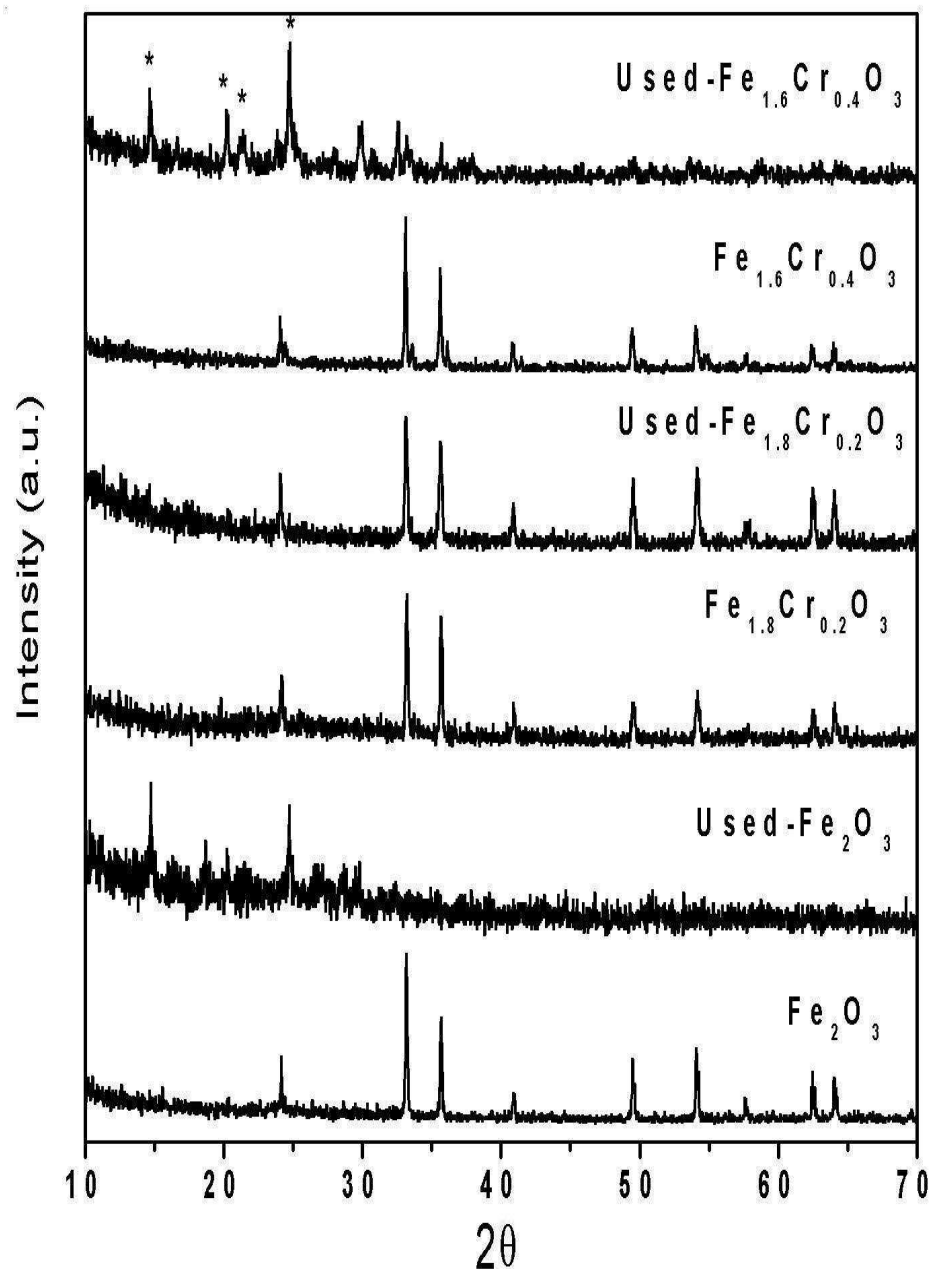
IR spectrum of effluent stream recorded during sulfuric acid decomposition over $\text{Fe}_{1.8}\text{Cr}_{0.2}\text{O}_3$ at various temperatures

Gas Chromatography



Temperature dependent catalytic activity for decomposition of sulfuric acid reaction using samples

XRD of fresh and used catalyst

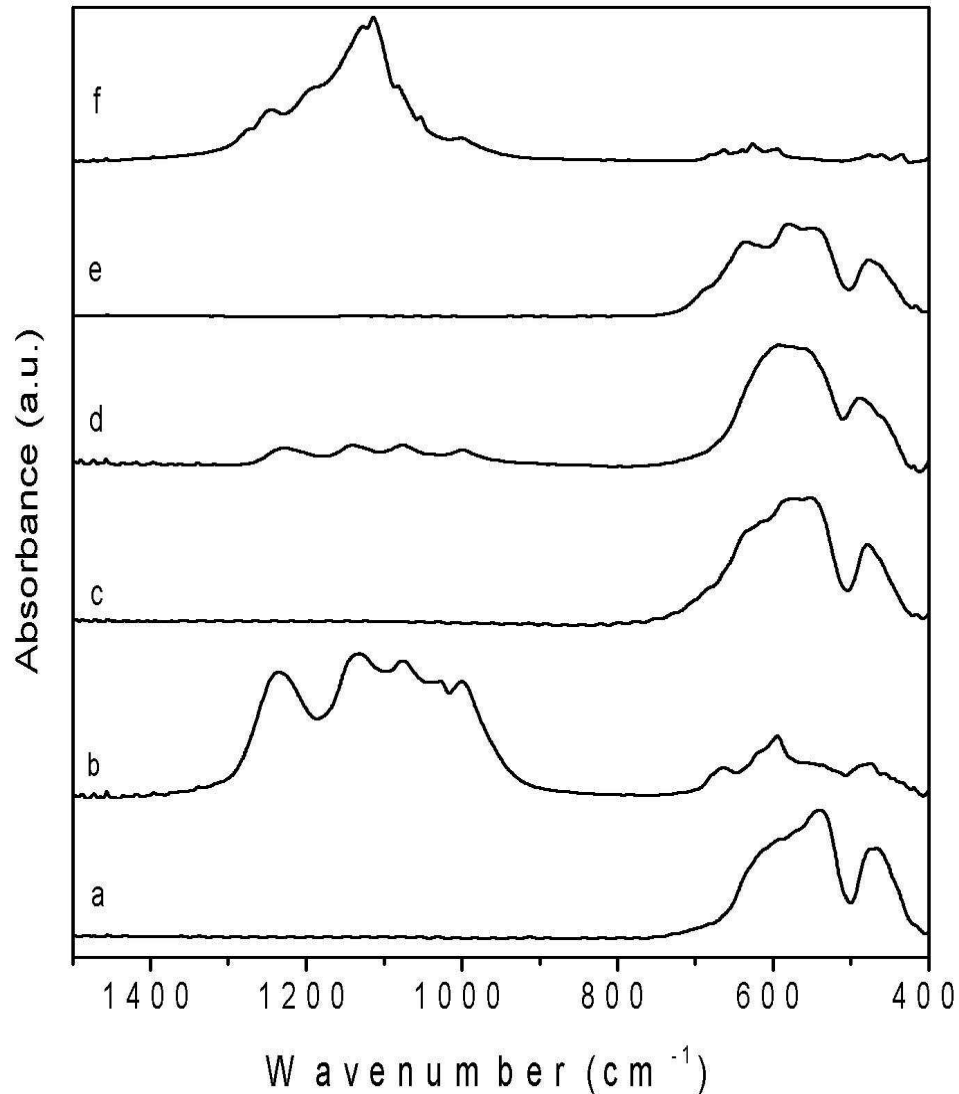


* - Lines due to $\text{Fe}_2(\text{SO}_4)_3$

Used Fe_2O_3 and $\text{Fe}_{1.6}\text{Cr}_{0.4}\text{O}_3$:
formation of bulk metal sulfates
(JCPDS. card No. 47-1774).

Used $\text{Fe}_{1.8}\text{Cr}_{0.2}\text{O}_3$ sample:
Lines due to $\text{Fe}_2(\text{SO}_4)_3$ are absent

IR spectra of fresh and used catalysts



New lines in the range of 1000-1200 cm⁻¹, can be assigned to SO bond stretching in metal sulphates

Used Fe₂O₃ and Fe_{1.6}Cr_{0.4}O₃ :
strong lines in 1200-1000 cm⁻¹

Used Fe_{1.8}Cr_{0.2}O₃ sample:
Weak lines in this region

Surface formation of metal sulphates in 10% substituted sample.

FTIR spectra of fresh (a, c, e) and used (b, d, f) catalyst samples in KBr
(a,b) - Fe₂O₃, (c,d) - Fe_{1.8}Cr_{0.2}O₃, (e,f) - Fe_{1.6}Cr_{0.4}O₃.

Plausible Mechanism

**Thermal analyses of metal sulfates
& the activity of the corresponding metal oxides**

Metal sulfate formation:



Decomposition of metal sulfate:



The presence of sulfate species on the used oxide samples such as Fe_2O_3 and $\text{Fe}_{1.6}\text{Cr}_{0.4}\text{O}_3$ confirms the above mechanistic aspect

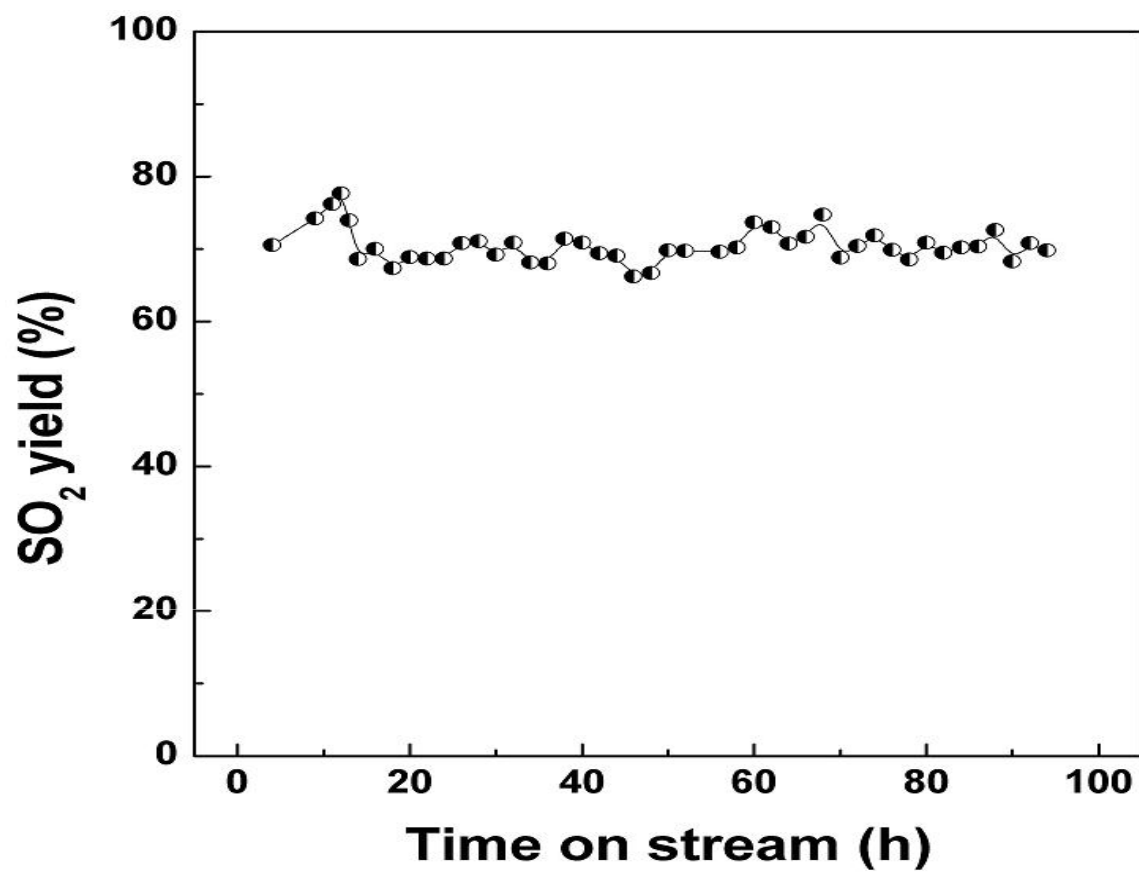
Successive TPR/TPO studies reveal better sintering characteristics for chromium substituted sample.

Lesser deactivation of the $\text{Fe}_{1.8}\text{Cr}_{0.2}\text{O}_3$ catalyst during use in sulfuric acid decomposition reaction suggest it as a promising, active and stable mixed oxide catalyst for the above reaction

Catalytic decomposition of sulfuric acid on mixed Cr/Fe oxide samples and its application in sulfur–iodine cycle for hydrogen production

International Journal of Hydrogen Energy, 33 (2008) 319-326

A.M. Banerjee, M.R. Pai, K. Bhattacharya, A.K. Tripathi, V.S. Kamble, S.R. Bharadwaj and S.K. Kulshreshtha



Time dependent SO₂ yield of Iron oxide catalyst for Sulfuric acid decomposition at 1073 K using a flux of 0.6 ml min⁻¹

Catalyst Preparation

Fe_2O_3 was prepared from metal nitrate solution by co-precipitation route.

The powder was made into granules of 3-5mm diameter.

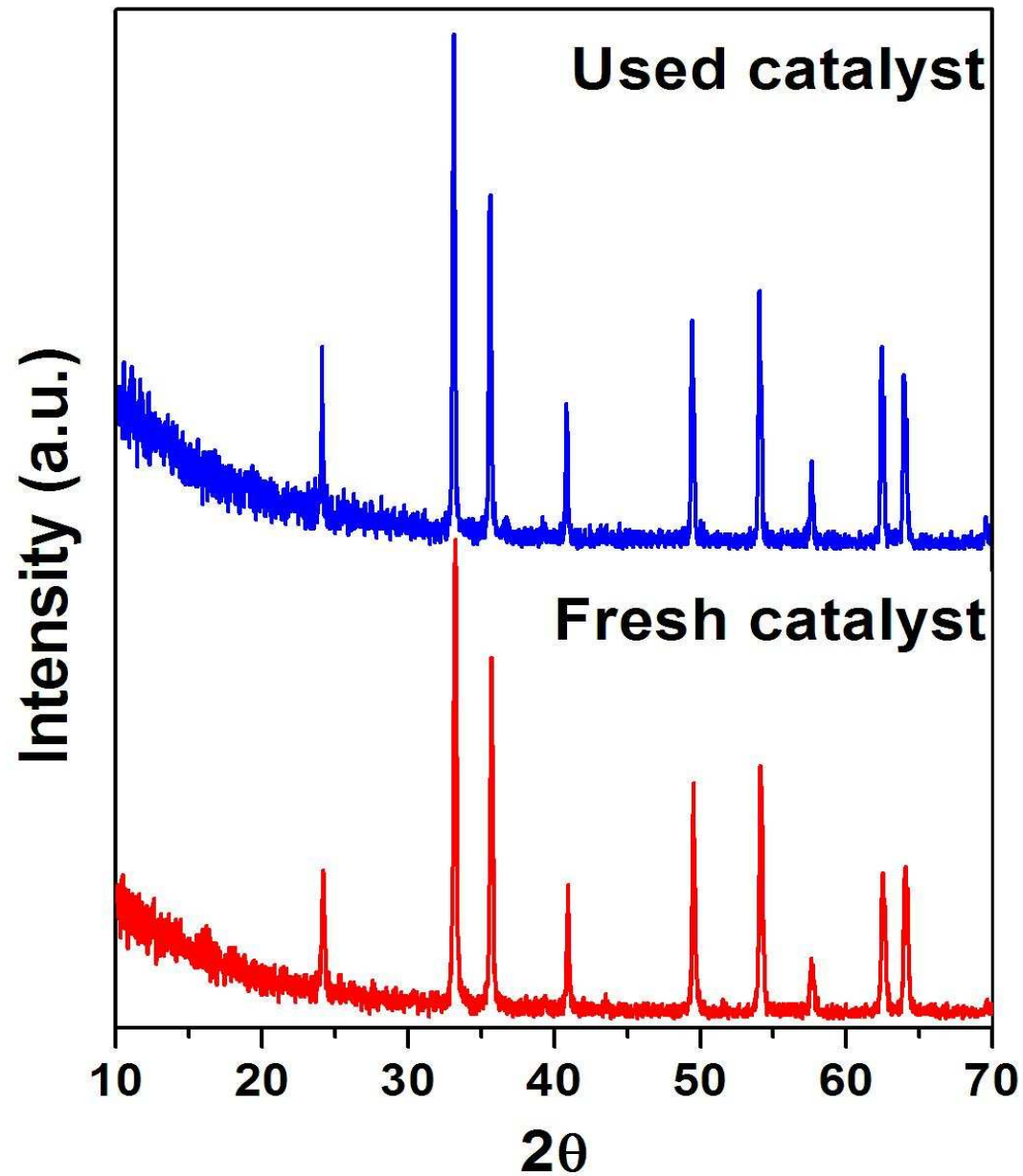
Activity Evaluation :

20gm Catalyst

**Flow Rate:~ 700 mlhr-1gm-1
(0.56ml/min of liq H_2SO_4)**

No N_2 flow as diluent

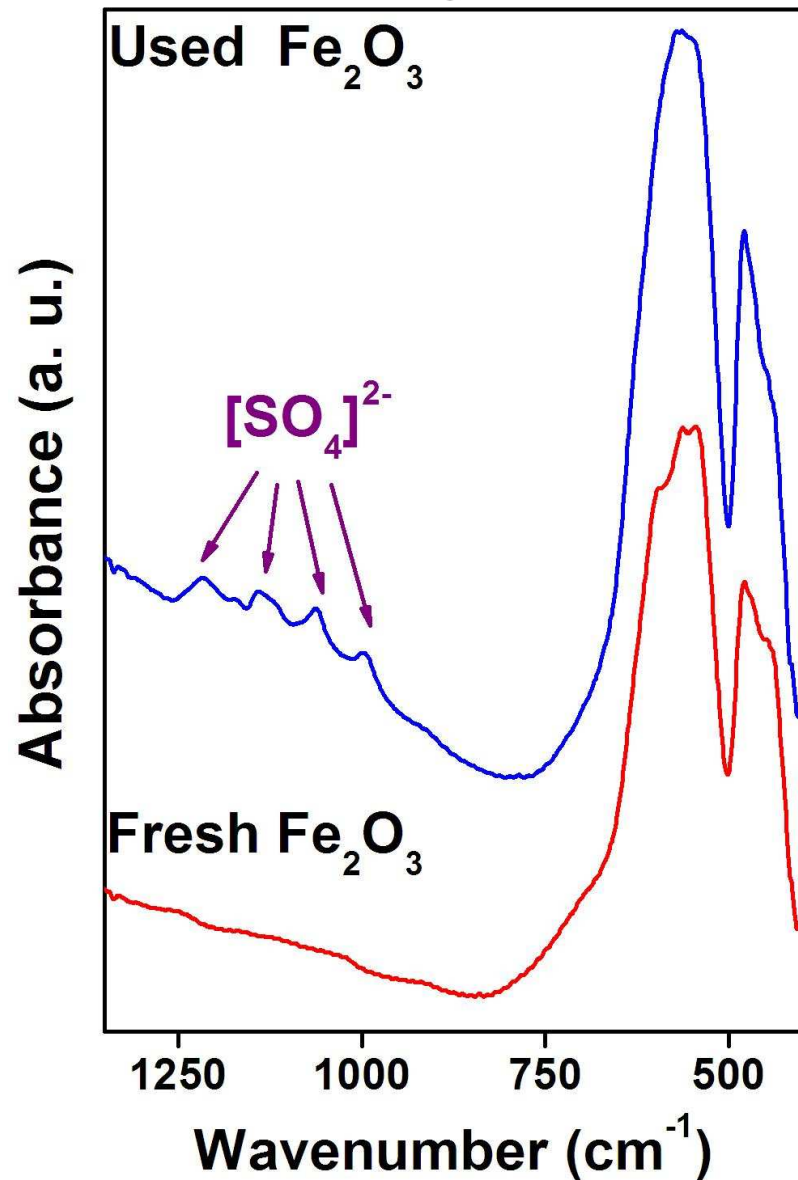
XRD



XRD patterns of the used and fresh catalyst sample are similar

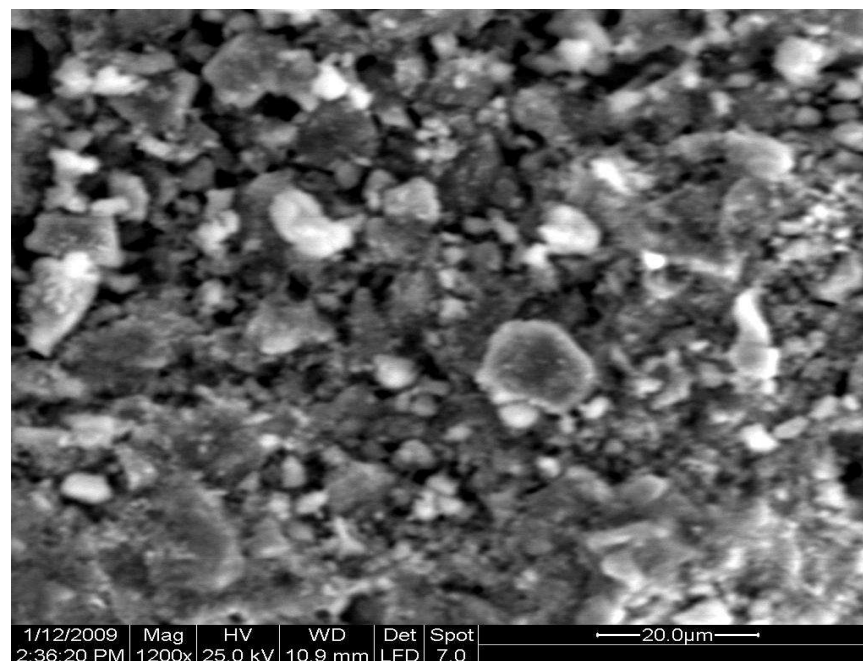
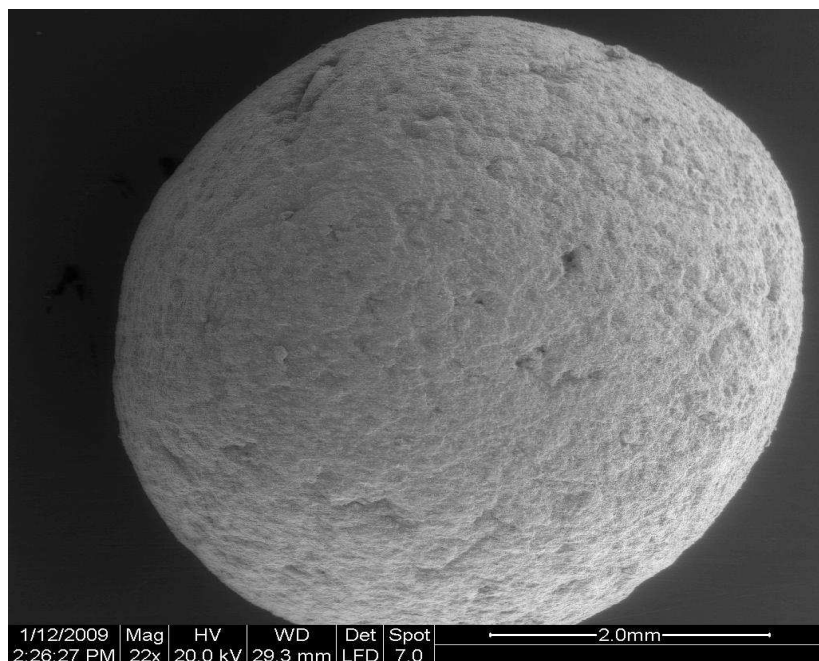
Stable: No Phase Change

IR

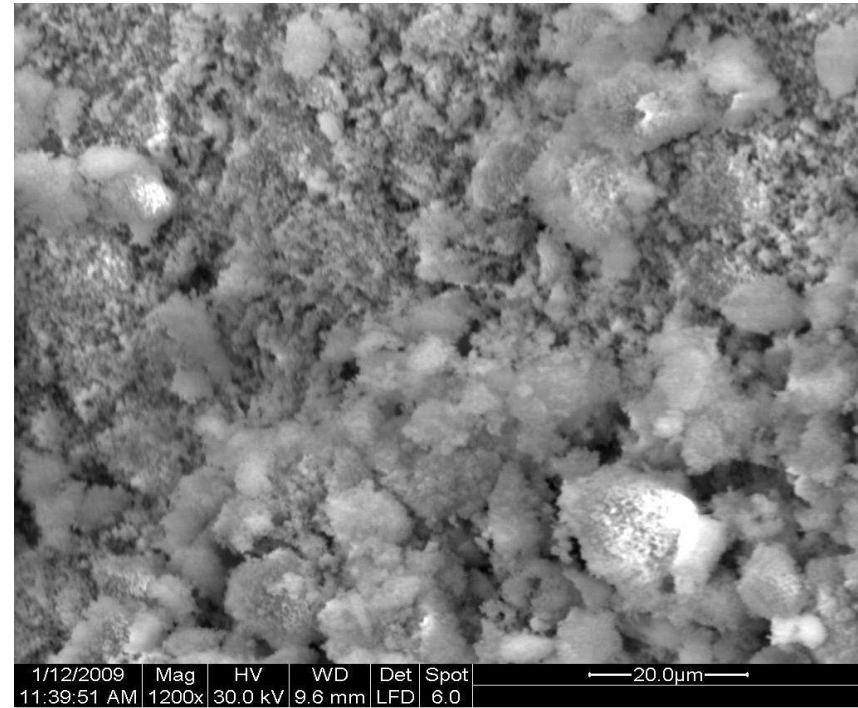
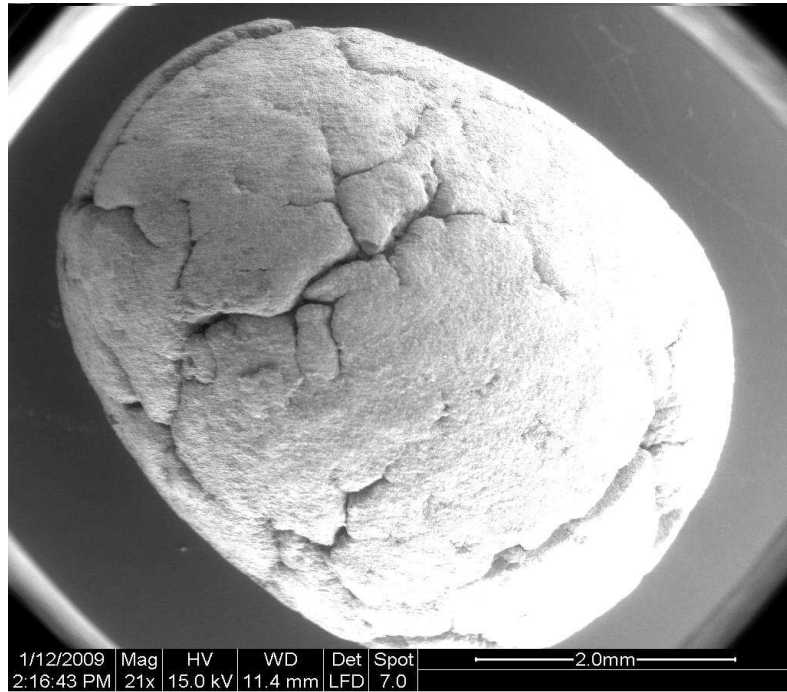


FTIR spectra of fresh and used catalyst samples

IR lines in the range of 1000–1200 cm⁻¹ can be assigned to SO bond stretching in metal sulfates.



SEM micrographs of Fresh Fe₂O₃ catalyst



SEM micrograph of used catalyst Fe_2O_3

Conclusions

New Quartz apparatus based on a dual-tube integrated Sulfuric Acid Boiler/Decomposer was developed and sulfuric acid decomposition was successfully operated at 700 to 825°C.

Conversion rates achieved using Fe_2O_3 catalyst are close to thermodynamic predictions.

Long-term (100hrs) stability test was conducted where there was no deterioration in the catalytic activity.

No bulk but evidence of surface sulfate formation confirms their formation and decomposition as the rate determining step in the mechanism of $\text{SO}_3 \rightarrow \text{SO}_2$ conversion on Fe_2O_3 .

Thus, Fe_2O_3 can be identified as stable, highly active catalysts for sulfuric acid decomposition which provides an extremely harsh environment for catalytic materials

SUMMARY

The 2010s decade could well mark the beginning of the “Hydrogen Age”

The predominant existing process for large scale hydrogen production is Steam - Methane Reforming (SMR)

SMR is a carbon based technology that emits a primary greenhouse gas - Carbon dioxide

In contrast, nuclear based hydrogen production does not emit greenhouse gases

Nuclear heat can be supplied abundantly for large scale hydrogen production by water splitting

Nuclear energy for hydrogen production is an innovative “green” idea that can take a significant step towards

saving modern society from climate change

and irreversible damage to worldwide ecosystems

Thank You